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OF

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Vol. XLVI.

1884. ABSTRACTS.

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LONDON:

J. VAN VOORST, 1, PATERNOSTER ROW.

1881

LONDON :

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY,  
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# JOURNAL

OF

## THE CHEMICAL SOCIETY.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

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### General and Physical Chemistry.

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**Infra-red Radiation Spectra.** By H. BECQUEREL (*Compt. rend.*, **97**, 71—74. Compare also Abstr., 1883, 761).—The author has examined the infra-red radiation spectra of several metals by the method previously described (*Compt. rend.*, **96**, 121).

*Sodium* gives two strong lines of wave-lengths 18190 and 10980, coincident with two lines in the solar spectrum. The line at 8190 can be seen with an ordinary spectroscope, and coincides with Brewster's solar line Y.

*Magnesium* gives three strong lines at 8755, 10300, and 11300 respectively, coincident with three lines in the solar spectrum.

*Calcium* in the electric arc gives a strong band of mean wave-length about 8480, coincident with a group of lines in the solar spectrum.

*Potassium* gives five strong lines at 7700, 10030, 10730, 11250 and 11820 respectively.

*Silver* gives two very strong lines at 7720 and 8290 respectively.

*Thallium* gives a very strong line at 11050, very near the second sodium line, but much stronger than, and quite distinct from, the latter.

The infra-red region of the spectrum down to about wave-length 8600 can be seen with an ordinary spectroscope by concentrating the light on the slit and filtering out the more luminous rays by means of a solution of iodine in carbon bisulphide.

C. H. B.

**Copper Oxide Battery.** By F. DE LALANDE and G. CHAPERON (*Compt. rend.*, **97**, 164—166).—The elements of the battery are zinc, cupric oxide, and potassium hydroxide. The cupric oxide is in contact with a plate of iron or brass which forms the positive pole, or

the outer vessel of the battery is constructed of one of these metals. The cupric oxide is the depolarising element of the battery, and is reduced to metallic copper, its conductivity increasing therefore as the battery is used. The electromotive force of this cell is about one volt, and its internal resistance is very low and does not sensibly alter while the battery is in action. Small sizes give a current of two ampères; large sizes give as much as 30 ampères. Since the potash solution has no action on the oxide of copper nor on the amalgamated zinc, there is no waste when the battery is not in action. The reduced copper can be reconverted into oxide by roasting. This battery can be used for long periods through low resistances, since depolarisation is rapid and complete.

C. H. B.

**Currents Produced by Immersion and Emersion, and by the Movement of a Metal in a Liquid.** By KROUCHKOLL (*Compt. rend.*, **97**, 161—163).—It has been known for some time that if two electrodes of the same metal are immersed in a liquid and one of them is moved, the motion produces a current the direction of which depends on the nature of the metal and liquid. If, too, one of the electrodes is placed in the liquid and the other is immersed afterwards, a current is produced at the moment of immersion.

The author finds that a current is also produced when one of the electrodes is withdrawn from the liquid. The current at immersion is in the opposite direction to that produced by movement of the electrode in the liquid; the current of emersion is in the same direction as the current produced by movement. These immersion and emersion currents are produced when the metal is passed from an insulating to a conducting liquid, as well as when the metal passes from the air into a liquid. The electromotive force produced by motion is analogous to that produced by polarisation: it is destroyed by solutions of salts of the metal of which the electrodes are composed, so that if the saline solutions are sufficiently strong, no current is produced by moving the electrode. These phenomena can be explained by Helmholtz's hypothesis of double layers of electrical tension.

C. H. B.

**Determination of the Limits of Electrolysis.** By C. TRUCHOT (*Compt. rend.*, **97**, 92—93).—Since the electromotive force required to decompose a given compound depends on the heat of formation of the compound, it follows that a determination of the minimum electromotive force necessary to produce decomposition, furnishes a measure of the heat of formation of the particular compound. The author employs a small Gramme dynamo, with a Jamin magnet, driven by a Smidt's water-motor fitted with a special regulating apparatus. The electromotive force is practically proportional to the velocity of the rotation of the dynamo, and this velocity can be regulated within very narrow limits. The actual electromotive force is determined by a volt-meter graduated by means of a Daniell element. Determinations of the minimum electromotive force required to electrolyse water, potassium sulphate, and other compounds, agree very closely with thermochemical determinations.

C. H. B.

**Pyro-electricity of Blende, Sodium Chlorate, and Boracite.**

By C. FRIEDEL and J. CURIE (*Compt. rend.*, **97**, 61—66).—Crystals of the cubical system which show tetrahedral hemihedrism behave like crystals of the hexagonal system. If heated or cooled regularly, *i.e.*, so that the expansion or contraction is equal along all the axes of hemimorphism, there is no development of pyroelectricity, but if the heating or cooling is irregular, so that tension is produced in different parts of the crystal, then electricity is developed. These phenomena have been observed with blende and with sodium chlorate. Mallard has shown that boracite at ordinary temperatures belongs to the rhombic system, but at about  $265^{\circ}$  its form changes to one belonging to the cubical system. The authors find that if a plate of boracite cut parallel with one of the tetrahedral faces is heated at  $300-320^{\circ}$  for some time and then allowed to cool regularly, no electricity can be detected until the temperature falls to about  $265^{\circ}$ , but at this point there is a considerable development of electricity, which gradually diminishes in intensity and eventually changes in sign. It appears therefore that when boracite cools regularly it only becomes pyroelectric at the point at which it ceases to belong to the cubical system.

C. H. B.

**Melting Points of Salts.** By E. MAUMENÉ (*Compt. rend.*, **97**, 45—48).—Pure potassium nitrate melts at  $327^{\circ}$ ; pure sodium nitrate at  $298^{\circ}$ . The following table gives the melting points of various mixtures of these and other nitrates as calculated and as observed:—

		Calculated.	Observed.	Difference.
3KNO <sub>3</sub>	+ NaNO <sub>3</sub>	320.7	265—247°	—55.7— 73.7°
2KNO <sub>3</sub>	+ NaNO <sub>3</sub>	318.4	265—244	—55.7— 74.4
KNO <sub>3</sub>	+ NaNO <sub>3</sub>	313.8	265—219	—55.7— 94.8
KNO <sub>3</sub>	+ 2NaNO <sub>3</sub>	308.8	242—224	—66.8— 84.8
KNO <sub>3</sub>	+ 3NaNO <sub>3</sub>	306.2	267—237	—39.2— 69.2
KNO <sub>3</sub>	+ AgNO <sub>3</sub>	246.8	169—121	—77.8—125.8
1.68KNO <sub>3</sub>	+ AgNO <sub>3</sub>	262.5	191—131	—71.5—131.5
NaNO <sub>3</sub>	+ AgNO <sub>3</sub>	231.7	251.5°	+ 19.8°
2NaNO <sub>3</sub>	+ AgNO <sub>3</sub>	248.0	263.0	+ 15°
AgNO <sub>3</sub> + KNO <sub>3</sub>	+ NaNO <sub>3</sub>	258.5	190—130	— 68—128.5
NaNO <sub>3</sub>	+ Ca(NO <sub>3</sub> ) <sub>2</sub>	374 or 399*	235—216°	—158 or 183*

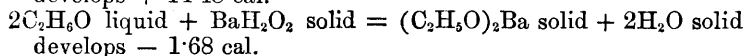
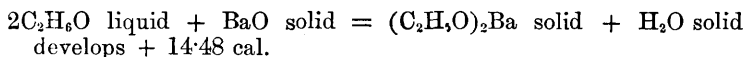
The first of the observed temperatures is the point at which crystals begin to form in the fused mixture, and the second is the point at which the whole mass becomes solid. The fall of temperature between these two points is perfectly gradual, and there is no fixed intermediate point which can be regarded as the true melting point of the mixture. The mixtures of sodium and silver nitrates do not show this irregularity, but have a definite melting point. Calcium nitrate, which cannot be fused alone without decomposition, melts readily when added in small quantities to fused sodium nitrate, and does not decompose. Zinc nitrate behaves in a peculiar manner. When a previously fused and resolidified mixture of sodium and calcium nitrates

\* According as the melting point of calcium nitrate is taken as  $450^{\circ}$  or  $500^{\circ}$ .

in equivalent proportions is added gradually to gently heated zinc nitrate, the fragments of the mixture decompose at a temperature as low as  $210^{\circ}$ , and decomposition continues so long as any of the fragments remain undissolved, but ceases when the whole mass becomes completely liquid. The same phenomenon is observed on each successive addition of the mixture. A mixture of the three nitrates in equivalent proportions solidifies at  $170^{\circ}$ , about  $80.5^{\circ}$  above the calculated melting point.

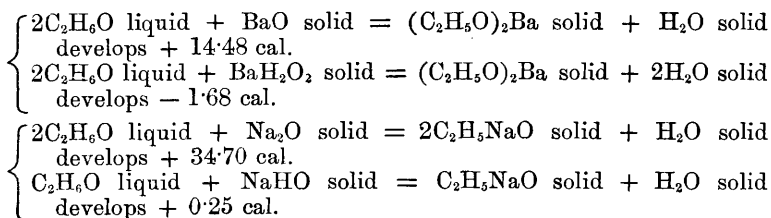
C. H. B.

**Barium Alcoholate.** By DE FORCRAND (*Compt. rend.*, **97**, 170—172).—Barium alcoholate is so readily decomposed by atmospheric moisture, that it is almost impossible to obtain it free from hydroxide, and in thermochemical determinations it is necessary to make a correction for this impurity. The heat of solution of the alcoholate at  $20^{\circ}$  is + 19.76 cal., from which it follows that—

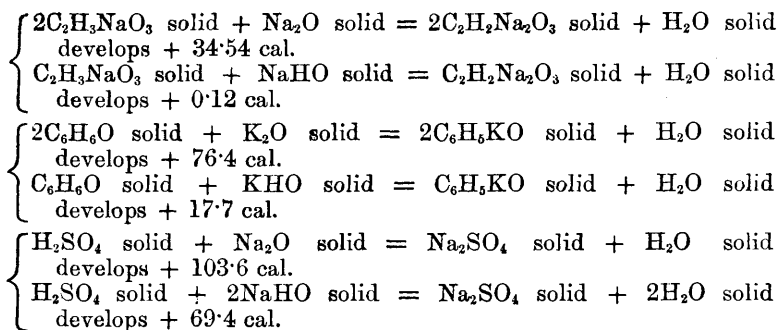


This development of heat is somewhat smaller than that produced by the hydration of barium oxide. The reverse reaction  $(\text{C}_2\text{H}_5\text{O})_2\text{Ba solid} + 2\text{H}_2\text{O liquid} = 2\text{C}_2\text{H}_6\text{O liquid} + \text{BaH}_2\text{O}_2 \text{ solid}$ , develops + 4.56 cal. These results explain the known properties of the alcoholate. In presence of excess of alcohol it is necessary to take into account the heat of solution of the alcoholate in alcohol and the formation of secondary alcoholates similar to those of sodium. The heat of solution in a large excess of alcohol is + 20 cal.; if a saturated solution is formed it is + 12.50 cal. By reason of the dissociation of the secondary alcoholates, an alcoholic solution of barium alcoholate always contains  $(\text{C}_2\text{H}_5\text{O})_2\text{Ba}$ . If such a solution is mixed with a small quantity of water, part of the alcoholate is converted into hydroxide, and the latter, being insoluble, is precipitated. The equilibrium of the system is thus disturbed, and the conversion of the alcoholate into hydroxide continues until all the water has been precipitated as barium hydroxide.

The following table shows the relative stability of the metallic derivatives of certain alcohols and acids with respect to water and acids. It is, however, also necessary to take into account the formation of secondary compounds (hydroxides, secondary alcoholates, basic salts, &c.), since the heat of formation of these bodies may change the direction of the reaction :—







C. H. B.

**Heat of Formation of Potassium Fluorides.** By GUNTZ (*Compt. rend.*, **97**, 256—258).—*Anhydrous Potassium Fluoride.*—The neutralisation of 1 mol. hydrofluoric acid (dilute) by potassium hydroxide (dilute) develops + 16·12 cal. The heat of solution of the anhydrous fluoride is 3·6 cal. These results agree with those of Thomsen and Favre respectively.

$\text{KHO solid} + \text{HF liquid} = \text{KF solid} + \text{H}_2\text{O solid}$  develops + 30·98 cal.

$\text{KHO solid} + \text{HF gas} = \text{KF solid} + \text{H}_2\text{O solid}$  develops + 38·22 cal.

*Crystallised Potassium Fluoride*,  $\text{KF}\cdot2\text{H}_2\text{O}$ .—Heat of solution  $-1\cdot03$  cal.: heat of hydration,  $\text{KF solid} + 2\text{H}_2\text{O, liquid} = \text{KF}\cdot2\text{H}_2\text{O solid}$ , develops + 4·63 cal.; with  $2\text{H}_2\text{O solid}$ , + 1·8 cal.

$\text{KHO solid} + \text{HF liquid} + \text{H}_2\text{O solid} = \text{KF}\cdot2\text{H}_2\text{O solid}$  develops + 34·17 cal.

$\text{KHO solid} + \text{HF gaseous} + \text{H}_2\text{O solid} = \text{KF}\cdot2\text{H}_2\text{O solid}$  develops + 41·41 cal.

The action of 1 mol. hydrofluoric acid on 1 mol. potassium fluoride in dilute solution is accompanied by an absorption of heat  $-0\cdot57$  cal.; a phenomenon similar to that observed in the case of hydrogen potassium sulphate. The heat of solution of potassium hydrogen fluoride,  $\text{KF}\cdot\text{HF}$  is  $-6\cdot01$  cal.

$\text{KF solid} + \text{HF gas} = \text{KF}\cdot\text{HF solid}$  develops + 21·04 cal.

$\text{KF solid} + \text{HF liquid} = \text{KF}\cdot\text{HF}$  „ „ + 13·80 „

$\text{KHO solid} + 2\text{HF gas} = \text{KF}\cdot\text{HF solid} + \text{H}_2\text{O solid}$  develops + 53·13 cal.

$\text{KHO solid} + 2\text{HF liquid} = \text{KF}\cdot\text{HF solid} + \text{H}_2\text{O solid}$  develops + 38·65 cal.

C. H. B.

**Compressibility and Liquefaction of Gases.** By J. JAMIN (*Compt. rend.*, **97**, 10—16; see also *Abstr.*, 1883, 898).—The author has represented the results of Andrews' experiments by a series of curves, the ordinates of which represent the density of the gas, and the abscissæ the pressure for the several temperatures  $13\cdot1^\circ$ ,  $21\cdot5^\circ$ ,  $31\cdot1^\circ$ ,

32.5°, 35.5°, at which the experiments were made. Below the critical point, the curve is at first slightly convex with respect to the axis  $x$ , because the density increases more quickly than the pressure, but at a certain point, B, the curve suddenly changes in direction. At this point, the gas has attained its maximum tension, and liquefaction commences, the curve continuing in the new direction until liquefaction is complete, when it suddenly takes a direction corresponding with a slow increase in density, this part of the curve being slightly concave because the compressibility gradually decreases. That this interpretation of the curve is correct is proved by the fact that the maximum tensions of the gas at the different temperatures correspond with the points B, B', B'', &c., at which the direction of the curve changes. Comparison of the different curves shows that the minimum density of the liquid at the moment of its formation is at first much higher than the maximum density of the gas when it begins to liquefy, but the difference between these two densities diminishes as the temperature rises, and at 35° the difference is *nil*, from which it follows that below 35° the liquid ought to form and separate from the gas by reason of its higher density, but above 35°, although the liquid is still formed, it cannot separate from the gas. The author has calculated the ratios between the density of the gas and the density of the liquid in Andrews' experiments, and also the coefficient of expansion between 31.1° and 35.5°. These coefficients are very high, and undergo remarkable changes. Between 75.6 and 76 atmos. the coefficient of expansion rises suddenly from 0.0821 to 0.2716, which can only be explained by supposing that at this pressure and at 31.1° the gas is really liquefied, although apparently gaseous, and when the temperature rises to 35.5° it again passes into the gaseous state. Again, between 82 and 83.4 atmos. the coefficient suddenly falls from 0.13114 to 0.0703, a fact which can only be explained by supposing that at this pressure and even at the higher temperature the gas is again liquefied, although apparently remaining gaseous. It would appear that the homogeneous mass in the vessel under these conditions is not really gaseous, because it has too high a density, nor yet really liquid, because it has a high coefficient of expansion and compressibility, but that it exists in an intermediate state. Detailed examination of the curves corresponding with temperatures above the critical point supports these views. The following table gives the successive increments of density due to successive equal increments of pressure:—

Atmos.	70	72	74	76	78	80	82	84	86	88	90	92	94	96	98	100
D'—D	—	10	11	12	13	31	38	72	27	15	13	9	8	7	7	5

It is evident that between 82 and 84 atmos. the gas is liquefied, and it is also evident that this change although very rapid is not abrupt. It becomes less rapid and takes place at higher pressures as the temperature rises. The results of Cailletet and Amagat's experiments with oxygen, hydrogen, and similar gases at high pressures are represented by curves similar to those representing Andrews' experiments above the critical point. In every case the curve is convex at low pressures and concave at high pressures, with an intermediate point of inflexion which, according to the author's view, is the point at

which the gas liquefies. The increments of density in Amagat's experiments with oxygen at  $0.3^{\circ}$  are given in the following table:—

Atmos.	20	30	40	50	60	70	80	90	100	110	120	130
D'—D	—	76	77	77	78	78	79	79	82	83	77	78

Atmos.	140	150	160	170	180	190
D'—D	78	78	77	76	75	75

It would appear that the oxygen really liquefies between 100 and 110 atmos., although the change is not so well marked as in the case of carbonic anhydride. The following table gives the points of inflexion and maximum compressibility (H) as determined by Amagat's experiments:—

	Point of inflexion.	H.
Oxygen .....	102 atmos.	130 atmos.
Methane .....	95 "	127 "
Ethylene.....	67 "	83 "
Nitrogen.....	55 "	109 "
Hydrogen .....	0 "	0 "

It is evident that at a higher temperature these points of inflexion and maximum compressibility will correspond with higher pressures, but at a sufficiently low temperature the point H will differ but little from the point of origin of the curve, and experiments will give only that portion of the curve beyond K, which always represents a diminishing compressibility; but this is actually observed in the case of hydrogen. It follows therefore that at the ordinary temperature, and under a pressure of 3—4 atmos., hydrogen has passed its point of inflexion, or, in other words, is really liquid. This conclusion is in accord with the law of continuity, and brings hydrogen, which has hitherto been regarded as an exception, under the general laws of the compressibility of gases.

C. H. B.

**Change of Volume of Metals and Alloys at Melting.** By E. WIEDEMANN (*Ann. Phys. Chem.* [2], 20, 228—243).—The author has made a series of experiments on the expansion of volume at melting point, and the relative rates of cooling of tin and certain alloys of bismuth and lead.

The dilatometer method was employed. The substance to be examined was enclosed in a closely fitting glass cylinder, at the upper end of which was fixed a capillary tube. The most convenient liquid for filling the apparatus was found to be oil, which has the advantage of not evolving air when heated to  $200^{\circ}$ ; moreover, it does not possess an appreciable vapour-tension at that temperature. When heated above that point the oil attacks the metal. The rate of cooling was determined by heating the metal to  $260^{\circ}$  in an iron vessel. A thermometer protected by a glass cap filled with oil was enclosed within the molten mass. The whole apparatus was then immersed in a double walled metallic vessel, the intermediate space between the walls being filled with water. The intervals of time required for cooling  $5^{\circ}$  were carefully measured; the reciprocal value

for these times may be taken as a measure for the velocity of cooling of the metal.

In three experiments, it was found that tin on melting expanded in volume 1.76, 1.69, 2.20 per cent. These results are in direct contradiction to those of Nies and Winkelmann, who melted a large quantity of the metals and then dropped in a solid fragment of the same metal, and observed whether this fragment floated or sunk. But the author points out that in this method it would be exceedingly difficult to avoid convection currents, which would be liable to carry up the solid fragments to the surface in the centre of the vessel. Experiments also proved that soft solder expands almost 2 per cent. of its volume in melting.

*Alloys of Bismuth and Lead.*— $\text{Pb}_2\text{Bi}$  of sp. gr. 11.4 begins to show an increase of expansion at about  $120^\circ$ — $136^\circ$ , which reaches its maximum at  $180^\circ$ . When heated to  $240^\circ$  and allowed to cool, the temperature remained constant for long intervals of time at  $180^\circ$  and  $125^\circ$ , the two melting points of the alloy.  $\text{BiPb}$ , sp. gr. 11.03, expands abnormally between  $127^\circ$  and  $132^\circ$ , melts at  $146^\circ$  and  $125^\circ$ .  $\text{PbBi}_2$ , sp. gr. 10.96, expands abnormally between  $126^\circ$  and  $132^\circ$ , melts at  $140^\circ$  and  $124^\circ$ .  $\text{PbBi}_4$ , sp. gr. 9.73, expands most markedly between  $120^\circ$  and  $136^\circ$ , melts at  $125^\circ$  and  $200^\circ$ .  $\text{PbBi}_8$ , sp. gr. 8.6, melts partially between  $125^\circ$  and  $130^\circ$ , contracts between  $172^\circ$  and  $204^\circ$ ; its melting points are  $170^\circ$  and  $120^\circ$ . The results of these experiments show that these alloys contain a definite compound of composition between  $\text{PbBi}$  and  $\text{PbBi}_2$ , whose melting point is about  $125^\circ$ , and in which the excess of one metal, lead or bismuth, as the case may be, dissolves. For equal increments of temperature, the proportion of the metal dissolved rapidly increases. From the changes of volume at temperatures above the first melting point one can conclude whether the metal in excess expands or contracts on melting. The experiments would seem to indicate an expansion of lead and a contraction of bismuth, a result in accordance with previous observations. For example, the alloy  $\text{PbBi}_8$  consists of an alloy of low melting point, in which the excess of bismuth dissolves; if it be gradually warmed to  $120^\circ$ , the alloy and the excess of bismuth expand regularly. At this temperature the alloy melts with marked expansion, and contains the solid bismuth in suspension; above that point, the bismuth gradually dissolves and melts, while the rate of expansion *pari passu* decreases.

V. H. V.

### Specific Volume of Saturated and Unsaturated Alkyl Salts.

By F. WEGER (*Annalen*, **221**, 61—107).—The author has made a series of determinations of saturated and unsaturated hydrocarbons and alkyl salts, in order to ascertain the differences of specific volume corresponding to known differences of molecular weight. The method adopted is that proposed by Kopp, with slight modifications; the dilatometer was not heated in a bath of liquid, but was wholly immersed in the vapour of some volatile liquid. By this means corrections for the cool part of the dilatometer projecting outside the liquid, and its unequal heating from convection currents, are avoided. The readings were made with the naked eye, and a

TABLE I.

Name of Substance.	Method of Preparation.	$\alpha$ - <sup>4</sup> .	$b$ - <sup>6</sup> .	$c$ - <sup>9</sup> .
Ethylbenzene, $C_8H_{10}$ .....	Ethyl and phenyl bromides with sodium.	8.6172	2.3344	1.8319
Phenylethylene, $C_8H_8$ .....	Dibromylhydrocinnamic acid and potash.	9.5069	1.1580	1.6704
Phenylacetylene, $C_8H_6$ .....	Ethyl $\alpha\beta$ -dibromopropionate and potash.	9.7275	1.0587	3.1491
Phenyl bromide, $C_6H_5Br$ .....	Bromine on benzene.....	8.3368	0.90506	2.8245
Acetylene dibromide, $C_2H_2Br_2$ .....	Acetylene tetrabromide and zinc.	9.9103	1.7519	1.1776
Cinnamic acid, $C_9H_8O_2$ .....	From storax.....	6.9205 ( $t-133$ )	1.6428 ( $t-133$ )	—
Methyl cinnamate, $C_{10}H_{10}O_2$ .....	Cinnamic acid and methyl alcohol.	7.5009 ( $t-36$ )	1.0053 ( $t-36$ )	4.8163 ( $t-36$ )
Ethyl cinnamate, $C_{11}H_{12}O_2$ .....	Cinnamic acid and ethyl alcohol.	8.007	0.80135	1.1530
Propyl cinnamate, $C_{12}H_{14}O_2$ .....	Cinnamic acid and propyl alcohol.	8.4152	0.58474	1.3206
Phenylpropionic acid, $C_9H_{10}O_2$ .....	Cinnamic acid and sodium amalgam.	7.0048 ( $t-48.9$ )	1.8069 ( $t-48.7$ )	—
Methyl phenylpropionate, $C_{10}H_{12}O_2$ .....	As methyl cinnamate.....	8.5515	0.31368	4.802
Ethyl phenylpropionate, $C_{11}H_{14}O_2$ .....	As ethyl cinnamate.....	9.2504	0.099212	3.5974
Propyl phenylpropionate, $C_{12}H_{16}O_2$ .....	As propyl cinnamate.....	9.3098	0.05036	3.1061
Methyl acrylate, $C_4H_6O_2$ .....	Methyl dibromopropionate with zinc and sulphuric acid.	13.589	1.3342	31.235
Ethyl acrylate, $C_6H_8O_2$ .....	As the methyl salt.....	12.414	0.77929	16.71
Propyl acrylate, $C_8H_{10}O_2$ .....	do. do. ....	11.584	1.186	6.5399
Ethyl propionate, $C_6H_{10}O_2$ .....	Silver propionate and ethyl iodide.	—	—	—
$\alpha\beta$ -Dibromopropyl alcohol, $CH_2Br.CHBr.CH_2OH$ ...	Allyl alcohol and bromine...	7.4036	0.17744	7.8943

TABLE I.—*continued.*

Name of Substance.	Method of Preparation.	$a^{-4}$ .	$b^{-6}$ .	$c^{-9}$ .
Methyl $\alpha\beta$ -dibromopropionate, $\text{CH}_2\text{Br}.\text{CHBr}.\text{COOMe}$	Oxidation of above compound with nitric acid, and then treated with methyl alcohol. As the methyl salt . . . . .	8.8998	0.15041	4.1201
Ethyl $\alpha\beta$ -dibromopropionate, $\text{CH}_2\text{Br}.\text{CHBr}.\text{COOEt}$ .	—	9.9128	1.0801	9.4009
Dimethyl oxalate, $\text{COOMe}.\text{COOMe}$ . . . . .	—	11.991 ( $t-54$ )	5.6231 ( $t-54$ )	22.178 ( $t-54$ )
Ethyl oxalate, $\text{COOEt}.\text{COOEt}$ . . . . .	—	10.030	0.27596	5.3698
Methyl ethyl succinate, $\text{C}_7\text{H}_{12}\text{O}_4$ . . . . .	Silver ethyl succinate and methyl iodide.	9.1446	1.6461	0.15924
Diethyl succinate, $\text{C}_8\text{H}_{14}\text{O}_4$ . . . . .	Silver succinate and ethyl iodide, succinic acid and alcohol.	10.354	40.999	3.8411
Trimethyl phosphate, $\text{Me}_3\text{PO}_4$ . . . . .	Silver phosphate and methyl iodide.	10.516	1.9105	13.351
Ethyl dimethyl phosphate, $\text{EtMe}_2\text{PO}_4$ . . . . .	Silver dimethyl phosphate and ethyl iodide.	9.5262	0.57662	7.7127

mirror to exclude errors of parallax. The boiling points were determined by Kopp and Pawlewski's methods. The tables on pp. 9, 10 and 11, contain a summary of the author's results. In Table I are given the reagents by which the several compounds were obtained, and the experimental values for  $a^{-4}$ ,  $b^{-6}$ ,  $c^{-9}$  in the general equation  $V = 1 + at + bt^2 + ct^3$ , representing the expansion of volume for increase of temperature. In Table II are the boiling points, sp. gr. at  $0^\circ$  and at boiling point, and the specific volumes deduced from the data.

TABLE II.

Name of Substance.	Boiling point.	Sp. gr. at $0^\circ$ .	Sp. gr. at b. p.	Specific volume.
Ethylbenzene .....	136.5	0.88316	0.7612	138.93
Phenylethylene .....	146.2	0.9251	0.7914	131.11
Phenylacetylene .....	141.6	0.94658	0.8032	125.8
Phenyl bromide.....	153.6	1.5203	1.308	119.7
Acetylene dibromide.....	109.4	2.2983	2.0352	91.72
Cinnamic acid .....	300	1.0364	0.90974	162.29
Methyl cinnamate.....	259.6	1.0415	0.83888	188.17
Ethyl       ".....	271	1.0662	0.82143	213.75
Propyl       ".....	285.1	1.0435	0.7917	239.43
Phenylpropionic acid .....	279.8	2.07115	0.8780	170.44
Methyl phenylpropionate .....	336.6	1.0473	0.83824	195.19
Ethyl phenylpropionate .....	248.1	1.0348	0.80182	221.48
Propyl phenylpropionate .....	262.1	1.0152	0.77886	245.96
Methyl acrylate.....	80.3	0.93788	0.87194	98.4
Ethyl       ".....	98.5	0.93928	0.81970	121.71
Propyl       ".....	122.9	0.91996	0.7847	144.95
$\alpha\beta$ -Dibromopropyl alcohol ....	219	2.1682	1.7535	123.96
Ethyl propionate.....	98.3	0.91224	0.79472	128.06
Methyl $\alpha\beta$ -dibromopropionate..	205.8	1.9777	1.614	151.99
Ethyl-       ".....	214.6	1.8279	1.4554	178.14
Propyl-       ".....	233	1.7014	1.3391	204.09
Methyl oxalate.....	163.3	1.1579	1.0039	117.26
Ethyl       ".....	186	1.103	0.87652	166.18
Dimethyl succinate.....	195.2	1.1162	0.912	159.72
Methyl ethyl       ".....	208.2	1.0925	0.86482	184.58
Diethyl       ".....	215.4	1.0592	0.82726	209.85
Trimethyl phosphate .....	197.2	1.2378	1.0019	139.45
Dimethyl ethyl phosphate.....	203.3	1.1752	0.95188	161.45

*Homologous Compounds.*—On comparing the specific volumes of homologous compounds of analogous composition, it is found that the difference of specific volume for every  $\text{CH}_2$  is very variable. In the case of the ethereal salts of phosphoric acid, the difference is equal to Kopp's average value, 22; for the alkyl salts of the acids of the acetic and acrylic series, the difference is rather greater than 23; for those of the succinic, phenylpropionic, and acrylic acids it varies from 25—26. In the homologous alcohols, the specific volume for the  $\text{CH}_2$  group is about 20. Although the volume for  $\text{CH}_2$  varies with different series of compounds, yet it is practically

constant for various alkyl salts of one and the same acid, although not for corresponding ethereal salts of homologous acids. Thus, for example, the volume difference between ethyl oxalate and methyl ethyl succinate is not equal to that between methyl ethyl and ethyl succinate. Facts such as these cause questions to be raised as to the precise definition of homologous compounds.

*Isologous Compounds.*—Similarly on comparing the results obtained for saturated and unsaturated compounds, the difference in specific volume for  $H_2$  or  $nH_2$  varies from 5 to 9 or some multiple of these numbers. The observations of the author in this respect are in accordance with those of Buff, Zander, and Schiff.

Thorpe assigned the number 53.48 as the molecular volume of bromine (this Journal, Trans., 1880, 384); in the author's results, differences of  $Br_2$  in isologous compounds, as allyl and dibromopropyl alcohols, correspond with differences of specific volume varying from 49.96 to 59.14. Similar variations in the differences of specific volume corresponding with uniform differences of  $C_6H_4$  and  $C_2H_2Br_2$  in the molecule are also observable.

The specific volume values of the aromatic compounds examined by the author were found to be greater than the values calculated according to Kopp's general rules. V. H. V.

**Law of Smallest Volumes.** By W. MÜLLER-ERZBACH (*Annalen*, 221, 125—132).—In this communication, the author adduces further arguments in support of his law that in any chemical reaction the elements tend to arrange themselves in those forms of combination which occupy the smallest volume, or that greater condensation is correlated with greater affinity (comp. Abstr., 1882, 137, 451, 1024).

For example, the sum of the volumes of the trichlorides of phosphorus and boron plus three atoms of bromine, or of silicon tetrachloride plus four atoms of bromine, is greater than the sum of the volumes of the tribromides of phosphorus and boron plus three atoms of chlorine, or of silicon tetrabromide plus four atoms of chlorine.

Again, the experiments of Kämmerer (*Ann. Phys. Chem.*, 138, 290) have proved that hydrated chloric acid,  $HClO_3 \cdot 7H_2O$ , occupies a molecular volume of 164.4, and hydrated iodic acid,  $H_2O_3 \cdot 9H_2O$ , of 158.9; if to the molecular volume of chloric acid the number 36, or the molecular volume of two molecules of water be added, the volumes of chloric and iodic acid will be in the ratio of 200 to 159. According to the author's law, iodic should be more stable than chloric acid, and the experiments of Serullas have shown that an aqueous solution of the former decomposes at  $40^\circ$ , whilst those of Gay-Lussac prove that only a partial decomposition of an aqueous solution of the latter commences at  $200^\circ$ . Kremers has demonstrated that there is an increase of volume when potash and soda are neutralised with nitric, hydrochloric, and sulphuric acids. The author has pointed out that this apparent discrepancy from his law may be explained by the greater affinity of the molecules of water for the acid and the alkali on the one hand than for the resultant salt on the other. Thus an expansion instead of a contraction is the final result. In this connection, the author cites the experiments of Ostwald, who proved that



the volume occupied by a given weight of water containing in solution an equivalent of potash is less than that occupied by the same weight of water plus one equivalent of potash taken separately. The same result holds good in the case of sulphuric acid and water. Hence it may be stated that the result of the neutralisation of potash and soda with nitric, hydrochloric, and sulphuric acids is a contraction of volume, but that this contraction is so masked by the presence of large quantities of water that an expansion is the final result.

V. H. V.

**Method of Correcting the Weight of a Body for the Buoyancy of the Atmosphere when the Volume is Unknown.** By J. P. COOKE (*Chem. News*, 48, 39—41).—It is well known that corrections for the buoyancy of the atmosphere are seldom made because of the great trouble attached to obtaining the required data, and from them the necessary correction. The author proposes to obviate these difficulties in the following manner:—Assuming that the atmosphere within the balance-case is dry, easily effected by open vessels of strong sulphuric acid, the only corrections required are for temperature and pressure. To effect this the author fixes on two standards, viz., 30 inches for the barometric pressure, and 27° C. (= 300° on the so-called “absolute scale”) for temperature: hence a variation of  $\frac{1}{10}$ th of an inch from this standard will cause a change of  $\frac{1}{300}$  in the resultant effect of the buoyancy of the air on the load and its counterpoise, and according to the law of Charles, the variation of 1° from 27° C. produces a similar change.

With these standards, corrections for temperature are made by reducing the barometric pressure to 27° C., and then by taking weighings of the object for which the correction is required under varying conditions of temperature and pressure: the difference in weight corresponding to  $\frac{1}{10}$ th of an inch variation in the barometer is easily found, and a constant for the object weighed is obtained by which the weights can be readily reduced to the standard 30-inch barometric pressure, after having reduced them to the standard temperature, 27° C. It is simply necessary to multiply the difference between 300 and the reduced barometric pressure, and add or subtract the product, as the case may be, from the observed weights. An example, chosen from an observation made by the author, will illustrate the mode of working. In the first column of the subjoined table the weights of the same object are given under the varying conditions registered in the subsequent columns, and in the last column the results of the application of the constant are given (there are 15 observations in the original):—

Weight of object.	Temperature of balance	Height of bar. in $\frac{1}{10}$ ins.	Height reduced.	Result.
87·3447	23·5° C.	297·6	301·1	87·3451
87·3419	22·6	305·2	309·6	87·3451
87·3464	29·4	297·9	295·5	87·3450

Greatest weight	87.3464	Barometer highest	309.6
Smallest     ,,	87.3419	,, lowest	295.5
Differences	00.0045		14.1

$$\therefore \text{Constant} = 4.5 \text{ mgrms.} \div 14.1 = 0.319 \text{ mgrm.}$$

In this way, the relative weight of even large vessels can be obtained to a  $\frac{1}{10}$ th milligram; of course there is a limit to the accuracy; however it is noteworthy that the accuracy of the method is proportional to the requirement, for the greater the bulk of the load, the more accurately can the "constant" be found. Great precision is required for measuring temperatures and pressures in the case of loads of large volume.

From the data obtained by these observations and from the known normal density of the air, the volume of the object can be calculated, and therefore the same constant may be made to serve roughly for any given volume; thus in the case cited above the volume of the object exceeds that of the weights by 75 c.c., and the weight varies 0.3 mgrm. for  $1^{\circ}\text{C.}$ , or  $\frac{1}{10}$ th inch pressure. Hence with a difference of volume = 100 c.c. the weight would vary 0.4 mgrm. for  $1^{\circ}\text{C.}$ , or  $\frac{1}{10}$ th inch pressure, and so on. It is obvious that if the volume of the load was very large, the balance might be used for measuring the variations in atmospheric pressure and temperature.

D. A. L.

## Inorganic Chemistry.

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**Density of Liquid Oxygen.** By S. WROBLEWSKI (*Compt. rend.*, **97**, 166—168).—A known volume of oxygen was liquefied at  $-130^{\circ}$  in a calibrated tube, and the volume of the liquid was compared with the volume of a known amount of carbonic anhydride liquefied in the same tube at  $0^{\circ}$ . The sp. gr. of the liquid oxygen was found to be 0.89 and 0.90; mean, 0.895. C. H. B.

**Active Oxygen.** By E. BAUMANN (*Ber.*, **16**, 2146—2152).—It has long been observed that substances which under ordinary conditions are not affected by oxygen, are yet oxidised in presence of other substances, which combine directly with the oxygen of the air. Besides examples of these changes which have been brought forward by Hoppe-Seyler, the author, and also Leeds, have observed that carbonic oxide when passed over damp phosphorus is oxidised by the ozone formed into carbonic anhydride. Remsen and Keiser (*Chem. Soc. J.*, 1883, 454) have repeated these experiments, but with negative results, and they attribute the formation of carbonic anhydride to the oxidation by the ozone of the carbon of the corks used in the apparatus. The author has accordingly repeated his experiments with an apparatus made entirely of glass, and has confirmed his

former results. In one case 36.6 mgrm. of carbonic anhydride were formed by the passage of 700 c.c. of carbonic oxide over phosphorus; this represents an oxidation of 2.6 per cent. of the carbonic oxide.

In connection with the explanation of the phenomena of oxidation put forward on the one hand by Hoppe-Seyler and Leeds, and on the other by Traube, the author considers that the former is more satisfactory: for firstly it is simpler; secondly, it explains the greater number of phenomena; and thirdly, Traube's hypothesis gives no account of the formation of ozone, hydrogen peroxide, and active oxygen by the slow oxidation of damp phosphorus in the air.

V. H. V.

**Conversion of Carbonic Oxide into Carbonic Anhydride by Nascent Oxygen.** By A. R. LEEDS (*Chem. News*, 48, 25—29).—The author refers to works which have been published in support of and against the theory that carbonic oxide is converted into carbonic anhydride during the oxidation of phosphorus in moist air; he then proceeds to describe the latest repetition of his original investigation in support of the theory. Sticks of phosphorus were put into a large flat-bottomed bottle, fitted with a well ground stopper, filled with water free from air and carbonic anhydride, and inverted in a pneumatic trough. Well washed carbonic oxide and air, in equal volumes, were now introduced, sufficient water being left in the bottle so as to partially cover the phosphorus. The stopper was put in while the neck of the bottle was still under water; the bottle was then reversed, and kept at a temperature of 24°. After six days the gaseous mixture was withdrawn from the bottle; and, the glass stopper being replaced by a cork saturated with paraffin, and fitted with the necessary tubes, the bottle was immediately inverted in a mercury trough, and a little mercury allowed to enter in order to cover the cork. The tubes were respectively connected with an aspirator and an air-supply free from carbonic anhydride; and the issuing gas was passed through baryta-water and potassium iodide solution. The baryta-water soon became turbid, and was subsequently tested in a carbonic anhydride apparatus, when the potash bulbs in connection therewith had increased 0.0155 gram after the decomposition. The tube passing into the barium hydrate became incrustated; the incrustation when treated with acid evolved carbonic anhydride. There was no iodine set free in the potassium iodide solution, and therefore no ozone could have been present. The author considers, therefore, that the above statement is now established by a rigid quantitative and qualitative analysis.

D. A. L.

**Liquid Nitrous Anhydride.** By R. H. GAINES (*Chem. News*, 48, 97).—The author observes that this gas condenses at + 14.4° under a pressure of 755 mm., and when the liquid is heated, ebullition begins at the same temperature. The pure liquid is dark green, but changes to blue on the addition of a very little water; the blue and green liquids are not readily miscible.

D. A. L.

**Preparation of Caustic Potash and Soda.** By LÖWIG (*Dingl. polyt. J.*, 248, 260).—According to Löwig, an intimate mixture of sodium or potassium carbonate and ferric oxide is exposed to a bright

red heat until the whole of the carbonic anhydride has been expelled. The resulting melt of sodium or potassium ferride is treated with water at 80—90°, the ferride being decomposed into caustic soda or potash and ferric oxide. The latter on drying is used for a further operation. D. B.

**History of the Preparation of Artificial Sodium Carbonate from Common Salt.** By DUMAS (*Compt. rend.*, 97, 209—214).—A historical summary, eulogistic of Leblanc. C. H. B.

**Dimorphism of Silver Iodide.** By MALLARD and LE CHATELIER (*Compt. rend.*, 97, 102—105).—It has been shown (*Bull. Soc. Min.*, 5, 214) that boracite belongs to the rhombic system at the ordinary temperature, but changes to the cubic system at about 265° with absorption of heat of 4.77 cal. for 1 gram, and retains this form up to the melting point. Potassium sulphate behaves in a similar manner, passing from the rhombic to the hexagonal system, and ammonium nitrate, which belongs to the rhombic system at the ordinary temperature, suddenly changes to the cubic system at about 127°. Silver iodide is dull red at a sufficiently high temperature, but is light yellow at the ordinary temperature, and Wernicke has shown that at 138—138.5° the colour *suddenly* changes from deep yellow to yellowish-white, or *vice versa*, according as the temperature is rising or falling. By examination with polarised light, the authors find that when the silver iodide is heated it suddenly passes from the hexagonal to the cubic system, the change taking place at about 146°, a temperature not very far removed from that determined by Wernicke. Measurements of the mean specific heat of the iodide between different limits of temperature, show that the passage from the hexagonal to the cubic system is accompanied by an absorption of heat of 6.8 cal. for 1 gram. According to Zepharovitch the ratio of the axes in the hexagonal form,  $h : a = 1.2294 : 1$ . In the cubic form, the ratio of the tertiary to the secondary axis will be  $h : a = 1.2247 : 1$ , from which it appears that the hexagonal form closely approaches the cubic form, and that at the point of change from one form to the other there must be contraction along the vertical axis, or expansion along the horizontal axes, or both. This contraction and expansion has been actually observed by Fizeau, and may be regarded as preparatory to the change of crystalline form. It follows from these facts that the cubical expansion of silver iodide ought to be normal above 146°, and Rodwell has observed that the iodide experiences a sudden and considerable contraction between 142° and 145.5°, but afterwards expands regularly up to the melting point.

C. H. B.

**Chlorides of Lime and Lithia.** By K. KRAUT (*Annalen*, 221, 108—124).—This communication contains no new experiments; the author merely controverts Lunge's experiments and deductions therefrom as to the constitution of bleaching powder and the so-called "chloride of lithia." V. H. V.

**Separation of Gallium.** By L. DE BOISBAUDRAN (*Compt. rend.*, 97, 66—67, 142—144).—*From Tellurium.*—The tellurium, which must be in the state of tellurous acid, is precipitated by hydrogen sulphide in the cold, in presence of a considerable quantity of free hydrochloric acid. The filtrate is concentrated if necessary, heated to boiling, and treated with a current of hydrogen sulphide, the precipitate of tellurium sulphide being filtered off.

*From Silicon.*—The solution is made strongly acid with hydrochloric acid (any free sulphuric acid having been previously neutralised), evaporated to dryness, and heated for some time at 120—125°. The residue is moistened with strong hydrochloric acid, and the evaporation and ignition repeated. The gallium is then dissolved out by boiling dilute hydrochloric acid, the solution filtered, and the silica washed, first with dilute hydrochloric acid, and finally with water; the last traces of gallium are removed from the silica by dissolving it in potassium hydroxide, acidifying with hydrochloric acid, and repeating the above treatment.

*From Molybdenum.*—(1.) The molybdenum is precipitated in the cold by hydrogen sulphide in presence of a considerable quantity of hydrochloric acid, the precipitate being washed with dilute hydrochloric acid saturated with hydrogen sulphide. The filtrate is heated for some time at about 70°, then boiled, and any precipitate which forms is filtered off. The second filtrate is concentrated, and again treated in the same way. (2.) The solution is supersaturated with ammonia, mixed with ammonium sulphide in excess, gently heated, and then acidified with hydrochloric acid, heated to expel hydrogen sulphide, and filtered. The filtrate is concentrated, the ammonium salts destroyed by heating with aqua regia, and the solution again treated with ammonium sulphide. The molybdenum sulphide is dissolved in aqua regia, and the precipitation repeated in order to remove the last traces of gallium. Before applying methods (1) and (2) chlorides and lower oxides of molybdenum must be oxidised by means of nitric acid, excess of the latter being expelled by boiling with hydrochloric acid. (3.) The solution is acidified with sulphuric acid, mixed with a slight excess of ammonium sulphate, and the gallium alum precipitated by concentrating the liquid and adding three or four times its volume of alcohol of 85°. The alum is purified by recrystallisation. In accurate analyses, the greater part of the molybdenum should be precipitated as sulphide by (1) or (2), then the greater part of the gallium removed as alum, the last traces being separated from the concentrated mother-liquor by (1) or (2).

C. H. B.

**Salts of Aurous Oxide: Colorimetric Estimation of Gold.** By A. CARNOT (*Compt. rend.*, 97, 169—170).—When an aqueous solution of hydrogen phosphide is added gradually to a very dilute solution of gold chloride, either alone or mixed with phosphoric or arsenic acid, a rose coloration is produced. It would appear that this rose coloration (this vol., p. 115) is not due simply to a complex compound of aurous oxide and ferric oxide, but is produced also by simple salts of aurous oxide, such as the phosphate or arsenate. The presence of ferric oxide apparently increases the stability of these salts, for if any

foreign salt is added to a solution of the rose-coloured compound free from iron, the rose-coloured compound becomes blue and yields a slight bluish precipitate, whereas in presence of iron a purple precipitate is formed, which can be dried at  $100^{\circ}$  without alteration.

This reaction furnishes a colorimetric method for the rapid approximate estimation of gold. The intensity of the tint given by the solution under examination is compared with that of solutions of gold containing different amounts of gold in a constant volume (100 c.c.) of liquid. To obtain comparable solutions, the neutral solution of gold chloride is mixed with a drop of hydrochloric acid, one or two drops of ferric chloride, and a few drops of arsenic acid, and then diluted to 100 c.c. A small quantity of zinc powder is added, the liquid agitated, allowed to clarify by standing, and the clear liquid decanted off. The mineral to be examined is finely powdered, dissolved in aqua regia, the solution diluted, filtered, evaporated twice to dryness after addition of a little nitric acid, and heated to dull redness. The residue is treated with chlorine-water, which leaves the ferric oxide undissolved, the solution is filtered, the chlorine expelled by boiling, and the solution treated as above.

C. H. B.

**Action of Hydrochloric Acid on Stannous Sulphide.** By A. DITTE (*Compt. rend.*, **97**, 42—45).—Dry hydrochloric acid gas has no action on crystallised stannous sulphide at the ordinary temperature, but on gently heating it, decomposition commences, and stannous chloride and hydrogen sulphide are formed.

Aqueous hydrochloric acid, even in dilute solutions, attacks crystallised stannous sulphide at the ordinary temperature, but the degree of concentration of the acid has great influence on the decomposition, the phenomena being similar to those observed by Berthelot in the case of galena (*Mécan. Chim.*, **2**, 562). Decomposition takes place with a solution containing 8.3 per cent. of acid; stannous chloride and hydrogen sulphide are formed, and after some time equilibrium is established under somewhat complex conditions.

When hydrogen sulphide is passed into a solution of stannous chloride, deep brown stannous sulphide may be produced, but in many cases the precipitate consists of brilliant reddish-brown micaceous plates of a stannous chlorosulphide, which is decomposed by hydrogen sulphide and by water. The heat of formation of this compound is probably intermediate between that of stannous chloride and that of stannous sulphide, and its more or less complete decomposition by water plays a part in the establishment of equilibrium. When hydrochloric acid is brought in contact with an excess of stannous sulphide, or when hydrogen sulphide is passed into a solution of stannous chloride, equilibrium is eventually established between the hydrogen sulphide and the hydrochloric acid, the relative proportions of the two bodies depending on the temperature. The conditions of equilibrium are complicated by the fact that the solubility of hydrogen sulphide in solutions of stannous chloride decreases as the concentration of the latter increases. If, therefore, a dilute solution of hydrochloric acid acts on stannous sulphide, a small quantity of hydrogen sulphide is liberated, and dissolves in the liquid without saturating it,

whilst at the same time a correspondingly small quantity of stannous chloride is formed. If, on the other hand, a current of hydrogen sulphide is passed into a strong solution of stannous chloride, in which the gas is almost insoluble, a small quantity of stannous sulphide is formed, and the hydrochloric acid which is liberated is sufficient to establish equilibrium with the small quantity of hydrogen sulphide by which the liquid is saturated. The greater part of the stannous chloride therefore remains unchanged. If, however, the experiment is arranged so that the proportion of free hydrogen sulphide is the same in both solutions, the proportion of hydrochloric acid will also be the same in both, and equilibrium will be established, although the two solutions contain very different amounts of stannous chloride. It would appear, therefore, that the stannous chloride plays a considerable, although mainly a mechanical, part in the establishment of equilibrium, by virtue of the fact that its presence diminishes the solubility of hydrogen sulphide.

No hydrochloride of stannous chloride appears to exist. When hydrochloric acid gas is passed over hydrated stannous chloride,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , the latter melts and yields an acid solution of stannous chloride, and a new hydrate,  $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ . The same hydrate is formed by the action of concentrated aqueous hydrochloric acid on the hydrate,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . The decomposition of stannous sulphide by hydrochloric acid is also materially affected by the temperature which not only accelerates the action of the acid, but at the same time diminishes the solubility of the hydrogen sulphide.

Hydrated stannous sulphide is attacked by hydrochloric acid at the ordinary temperature, decomposition taking place in more dilute solutions and with greater rapidity, than in the case of the anhydrous sulphide, although the products of the reaction and the conditions of equilibrium are the same in both cases.

Similar phenomena are observed with stannous selenide. Stannous telluride is decomposed when heated in a current of dry hydrochloric acid gas, but is not attacked by the aqueous acid in concentrated solutions.

C. H. B.

**Antimony Pentiodide.** By J. H. PENDLETON (*Chem. News*, **48**, 97).—Evidence of the existence of pentiodides of phosphorus and arsenic have been obtained (Abstr., 1881, 507; and *Chem. News*, **44**, 194), and the author has now investigated a pentiodide of antimony.

Pure antimony is fused with excess of iodine in an atmosphere of an inert gas in a sealed tube, and the mixture is kept well fused for an hour or two; the tube is then heated at  $130^\circ$  in a sulphuric acid-bath, one end which is cooled with water serving to collect the surplus iodine which distils off. The residue is a dark-brown crystalline mass, decomposable by water or long exposure to moist air. It melts at  $78\text{--}79^\circ$ , but is very unstable, readily undergoing decomposition when exposed to even a moderate increase of temperature. Analytical results correspond "pretty closely to the formula  $\text{SbI}_5$ ."

Several experiments were tried in which the temperature of the acid-bath and time of exposure were varied.

D. A. L.



**Chromic Acid and Hydrogen Peroxide.** By H. MOISSAN (*Compt. rend.*, **97**, 96—99). The dark-blue compound formed by the action of hydrogen peroxide on chromic acid is rapidly decomposed by water, but is much more stable in ethereal solution, the stability being, however, much diminished by the presence of a small quantity of alcohol. By using carefully purified ether and a solution of 50 grams of potassium dichromate per litre, it is possible to obtain at 0° an ethereal solution of the dark-blue compound containing 0.5 per cent. of chromium. This solution may be digested over calcium chloride, and can be kept for six or eight hours at 0° without undergoing sensible decomposition, but in time it decomposes, chromic acid being deposited on the sides of the tube. Dilute solutions are more stable than concentrated solutions. The ethereal solution when evaporated at -20° in a vacuum leaves a deep indigo-blue oily liquid, which readily redissolves in ether. In contact with sodium, it evolves hydrogen, and when only very gently heated it rapidly decomposes into oxygen and chromic acid. The volumes of oxygen and hydrogen given off correspond with the formula  $\text{CrO}_3, \text{H}_2\text{O}_2$ ; it would therefore appear that the blue substance is a compound of chromic acid and hydrogen peroxide. The ethereal solution, in contact with phosphoric anhydride or other dehydrating agents, is rapidly decomposed with evolution of oxygen. It is also decomposed by acids, bases, lead dioxide, carbon, manganese dioxide, red lead, mercuric oxide, and sodium: in the last case with evolution of a mixture of hydrogen and oxygen. The ethereal solution also bleaches the skin like hydrogen peroxide.

The blue compound cannot be obtained by the action of ozone on chromic acid, and it is only formed by electrolysis when hydrogen peroxide is also produced.

C. H. B.

**Reduction of Iron Oxide with Carbonic Oxide.** By R. AKERMANN and SÄRNSTRÖM (*Dingl. polyt. J.*, **248**, 291—239).—Experiments on the reduction of ferric oxide prove that it is readily converted into ferrosoferric oxide, and that magnetite parts with its oxygen to form ferrous oxide more easily than does ferrous oxide to yield metallic iron. One volume of carbonic oxide diluted with 20 volumes of carbonic anhydride reduces ferric oxide to ferrosoferric oxide at 450°. One part of carbonic oxide with 2.1 parts carbonic anhydride effects a similar reduction at 300—350°. By raising the temperature to 850—900° 1 volume of carbonic oxide to 2.6 volumes carbonic anhydride still reduces magnetite, but with the proportions of one to three this is no longer the case even at a temperature of 800°. Ferric oxide is easily reduced to magnetite in layers 2 mm. thick without any further reduction taking place so long as the gaseous mixture contains at least three volumes carbonic anhydride to one volume of carbonic oxide. Ferrous oxide is easily reduced to the metallic state at 850° when the ratio of carbonic oxide to anhydride is 1 to 0.4. Experiments were made to oxidise iron by heating it in mixtures of carbonic oxide and carbonic anhydride, the results were unsuccessful, however, as regards the production of ferrous oxide. The reducing power of an equivalent of carbonic oxide on ferrous oxide does not

equal the oxidising power of an equivalent of carbonic anhydride on iron. In both cases, however, an increase of temperature gives rise to increased action. To reduce magnetite at a temperature of  $350^{\circ}$  to ferrous oxide, the quantity of carbonic anhydride must not exceed two volumes to one of carbonic oxide. The authors find that for the production of 100 kilos. iron at least 64.3 kilos. of carbon in the form of carbonic oxide are required. Much less than this, however, is repeatedly employed in blast furnaces; it follows therefore that a reduction has taken place by the carbon as such, a reaction requiring a higher initial temperature than the reduction with carbonic oxide. In regard to the consumption of fuel, therefore, very little saving is to be anticipated.

D. B.

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## Mineralogical Chemistry.

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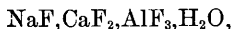
**Minerals of the Cryolite Group recently found in Colorado.** By W. CROSS and W. F. HILLEBRAND (*Amer. J. Sci.* [3], 26, 271—294).—Cryolite and several allied fluorides have been recently discovered in the Pike's Peak region, Colorado. The country rock of the whole district is a coarse reddish biotite granite of the Archæan formation.

The minerals described occur in two veins of massive white quartz, about one-third of a mile apart. In the vein designated A, cryolite, pachnolite, thomsenolite, gearksutite, prosopite, and, probably ralstonite appear. In vein B, prosopite, fluorite, and mixed fluorides appear intimately associated with zircon, kaolinite, and mica.

The *cryolite* from vein A is of a faint pink colour, and contains as a visible impurity the  $\text{Fe}_2\text{O}_3$  represented in the analysis—

$\text{Fe}_2\text{O}_3$ .	Al.	Ca.	Na.	$\text{H}_2\text{O}$ .	F.	Total.	Sp. gr.
0·40	12·90	0·28	32·40	0·30	53·55	99·83	2·972

Previous to the analysis by J. Brandl (Abstr., 1882, 1176) of *pachnolite*, carefully selected by Groth, pachnolite and thomsenolite were considered to possess the same chemical composition. The results of all earlier analyses agree very well with the formula



so that Brandl's analysis agreeing with the formula  $\text{NaF}, \text{CaF}_2, \text{AlF}_3$  caused great surprise. Groth explained the supposed anhydrous nature of pachnolite by assuming that the mineral analysed was largely contaminated with thomsenolite, but as the percentage of water never falls below 7 per cent. in any of the analyses published, this assumption necessitates a most improbable admixture of thomsenolite. All the analyses made by the authors correspond with the formula  $\text{NaF}, \text{CaF}_2, \text{AlF}_3, \text{H}_2\text{O}$ . The results of an analysis made upon crystals carefully identified as pachnolite by the rhombic section, were as follows:—

Al.	Ca.	Na.	H <sub>2</sub> O.	F.	Total.
12·36	18·04	10·25	8·05	(51·30)	100·00

Hence it appears that the pachnolite from Pike's Peak and thomsenolite are identical in chemical composition, unless the fact of all analyses of thomsenolite showing slightly more water than that required for the formula  $\text{NaF}, \text{CaF}_2, \text{AlF}_3, \text{H}_2\text{O}$ , may indicate a partial replacement of fluorine by hydroxyl.

In small cavities in the massive pachnolite, a mineral was found, occurring sparingly in a few specimens, which seemed to be different from any known species. The analysis gave—

Al.	Ca.	Mg.	K.	Na.	F.	Total.
11·40	0·72	0·22	28·94	9·90	46·98	98·16

from which may be deduced a formula analogous to that of cryolite, in which about two-thirds of the Na is replaced by K. The authors are of opinion that this mineral and *ralstonite* are not identical, but further investigations will be made as soon as better material can be obtained for examination.

*Gearksutite* is abundant among the minerals from this locality. It is made up of exceedingly minute colourless needles, and resembles kaolin in a remarkable degree. The analytical results obtained were as follows:—

Al.	Ca.	Na.	K.	H <sub>2</sub> O.	F.	Loss as oxygen.	Total.
15·31	22·30	0·10	0·04	15·46	42·07	4·72	100·00

In this Journal (Trans., 1883, 140) Flight described a mineral obtained from the cryolite bed of Greenland, which he considered new, and named *evigtokite*; but from the agreement of his analyses with those previously published, the similarity in occurrence and physical characteristics, there can hardly exist a doubt that Flight analysed *gearksutite*. The name *evigtokite* should therefore be dropped.

The rare mineral *prospite* is more frequent in vein B than in vein A. The analytical results obtained were as follows:—

Al.	Ca.	Mg.	Na.	H <sub>2</sub> O.	F.	Loss as oxygen.	Total.
22·17	17·28	0·17	0·48	13·46	33·18	13·26	100·00

B. H. B.

**Stibnite from Japan.** By E. S. DANA (*Amer. J. Sci.* [3], 26, 214—221).—In the size and beauty of the crystals, and in the great complexity of their form, the Japanese stibnite far exceeds specimens from other localities. The finest specimens known to the author are those recently acquired by the Yale Museum. They were obtained from Mount Kosang, near Seijo, in South Japan. They are of remarkable size. A simple group consists of two prismatic crystals, with vertical axes nearly parallel; the longer of the two measures 22 inches, and the other 15 inches in length, the thickness varies from  $1\frac{1}{2}$  to 2 inches. The lustre is very brilliant, and can be compared

only with that of highly polished steel. The complexity of form observed among Japanese stibnites is their most remarkable character. Previous to 1864 but 16 planes had been identified. Krenner (*Ber. Wien. Akad.*, 1864, 436) added 28 new planes, and Seligmann (*Jahrb. f. Min.*, 1880, 1, 135) added one more. Of these 45 planes, 30 have been observed on the Japanese crystals, and, in addition to these, 40 new planes have been determined, thus increasing the list to 85. This list could be considerably enlarged if the planes admitting of only doubtful determination were to be added.\* B. H. B.

**Gibbsite from Brazil.** By W. C. EUSTIS (*Chem. News*, 48, 98).—The specimen examined had a dark-coloured incrustation containing iron, a little manganese, and traces of nickel and cobalt. The mineral was greyish-white to nearly colourless, the surface was mammillary, and the structure radiate or fibrous. Lustre, sub-vitreous or slightly silky in some parts; hardness, 3; sp. gr., 2·4. Before the blowpipe it whitens, and loses water, but does not fuse. Analysis yielded the following results:—

Al <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	SiO <sub>2</sub> .	Total.
63·81	35·85	0·49	0·30	0·03	0·20	= 100·68

No aluminium phosphate could be detected.

D. A. L.

**Corundum Gems in India.** By C. U. SHEPARD (*Amer. J. Sci.* [3], 26, 339—340).—A remarkable deposit of sapphire and ruby has been discovered at Sungchang in the Himalaya Mountains. The matrix is a schistose or slaty rock, and the vein consists of quartz, amethyst, and several varieties of corundum, all beautifully crystallised. In addition to these, massive corundum, chlorite, and a little magnetite also occur. There is a great analogy in the mode of occurrence and other particulars between the crystals found in India and those produced at several of the American localities, notably at the Laurens district, S. Carolina; Pelham, Mass., and Burke Co., N. Carolina. The resemblances are, in fact, sufficiently important to lead to the belief that valuable corundum gems may yet be found in the United States. B. H. B.

**Cassiterite, Spodumene, and Beryl from Dakota.** By W. P. BLAKE (*Amer. J. Sci.* [3], 26, 235).—Cassiterite has been discovered in the central region of the Black Hills, Dakota, in a mass of coarsely crystalline granite. The felspar, quartz, and mica are in unusually large crystals; and, in addition to these minerals, there is an abundance of spodumene in gigantic crystals ranging from 2 to 6 feet in length, and 8 to 20 inches in diameter. In the midst of the spodumene and felspar crystals, the first masses of tin-ore were found. The chief associate of the tin-ore is a dense aggregation of small mica crystals. At another locality, where muscovite mica has

\* Since the above memoir was published, a much finer group of Japanese stibnite crystals has been purchased from Mr. Henson for the British Museum. The group consists of 120 crystals from 0·5 to 2·5 inches wide and 13 inches long; weight, 150 lbs.—B. H. B.

been mined, the author found large crystals of beryl embedded in quartz.

B. H. B.

**Descloizite from Mexico.** By S. L. PENFIELD (*Amer. J. Sci.* [3], 26, 361—365).—The mineral analysed was said to be from Zacatecas, Mexico. In all physical properties it seems to be identical with *tritochlorite* recently described by A. Frenzel (Abstr., 1882, 473). The analytical results obtained are given under I. Frenzel's analysis of tritochlorite is also given (II) for comparison:—

	V <sub>2</sub> O <sub>5</sub> .	As <sub>2</sub> O <sub>5</sub> .	P <sub>2</sub> O <sub>5</sub> .	PbO.	CuO.	ZnO.
I. ....	18.95	3.82	0.18	54.93	6.74	12.24
II. ....	24.41	3.76	—	53.90	7.04	11.06
	FeO.	H <sub>2</sub> O.	SiO <sub>2</sub> .	Total.	Sp. gr.	
I. ....	0.06	2.70	0.12	99.74	6.20	
II. ....	—	—	—	100.17	6.25	

The minerals have the same density, and are alike in many particulars, but it seems hardly probable that Frenzel could have overlooked 2.70 per cent. of water. The difference in the percentage of vanadic acid is also considerable.

B. H. B.

**Manganese Ores.** By M. LILL and L. SCHNEIDER (*Dingl. polyt. J.*, 248, 471).—The authors have analysed the following samples of manganese ores from Bukowina:—I. From Upper Arschitza; II. Lower Arschitza, and III and IV, from the mines Theresia and Schara. The following results were obtained:—

	I.	II.	III.	IV.
MnO.....	0.82	1.94	0.67	1.49
Mn <sub>2</sub> O <sub>3</sub> ....	8.20	7.60	8.79	7.01
MnO <sub>2</sub> ....	54.27	39.58	52.52	47.14
FeO.....	0.77	0.65	0.30	0.51
Fe <sub>2</sub> O <sub>3</sub> ....	16.71	27.34	16.27	12.78
Al <sub>2</sub> O <sub>3</sub> ....	0.46	1.73	2.02	0.85
CaO.....	1.08	1.03	1.80	3.50
MgO ....	0.47	0.28	0.30	0.57
BaO.....	traces	—	traces	—
CuO.....	traces	0.004	traces	0.006
Co .....	traces	traces	traces	—
Alkalis....	0.48	0.38	0.30	0.41
SiO <sub>2</sub> .....	10.95	13.00	10.90	18.10
SO <sub>3</sub> .....	traces	0.094	0.08	traces
P <sub>2</sub> O <sub>5</sub> .....	0.842	1.111	0.53	0.63
CO <sub>2</sub> .....	—	—	traces	0.18
H <sub>2</sub> O.....	5.25	5.55	5.25	6.50
	<hr/> 100.302	<hr/> 100.289	<hr/> 99.73	<hr/> 99.679

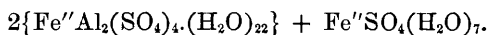
D. B.

**Native Ferrous and Aluminium Sulphate from Mexico.** By T. P. LIPPITT (*Chem. News*, 48, 98).—The specimen was a com-

pact mass of flexible fibres resembling asbestos. It was of a pale greenish-white colour, and had a silky shining lustre. Hardness, 2; sp. gr. 1·89. When heated in a glass tube, it gave off acid water. A small quantity of gypsum was intermixed with the mineral, which was otherwise quite homogeneous. The mineral is soluble in water, and yielded on analysis the following numbers:—

Fe (ferrous).	Al.	Ca.	SO <sub>4</sub> .	H <sub>2</sub> O.	Total.
7·81	4·92	0·52	41·59	43·60 =	98·44

The iron is all ferrous. Subtracting the constituents of gypsum from the results the formula  $\text{Fe}_3''\text{Al}_4(\text{SO}_4)_9(\text{H}_2\text{O})_5$  is obtained, which would be equal to a mixture of 2 mols. of halotrichite + 1 mol. melantrite.



D. A. L.

**Occurrence, Association, and Probable Mode of Formation of Barytes, Celestine, and Anhydrite.** By DIEULAFAIT (*Compt. rend.*, 97, 51—53).

*Barytes* is generally found associated with metallic ores containing sulphur, the metals present in these ores being antimony, arsenic, lead, silver, mercury, copper, cadmium, bismuth, zinc, and manganese. With the exception of the last two these metals have a strong attraction for sulphur; they are precipitated by hydrogen sulphide from acid solutions, and they are generally found in nature in the form of sulphides, which appear to be their most stable compounds. Zinc is frequently found as sulphide, but its most stable form is the oxide, although the tendency of the natural sulphide to pass into the state of oxide does not appear to be very great. The most stable form of manganese is the dioxide. Some of the sulphides with which barytes is associated are very volatile, others are decomposed when heated in presence of air (which generally has access to metallic veins), and all are decomposed when fused with alkaline chlorides. These and other facts show that the barytes and the minerals with which it is associated have never been subjected to the action of even a moderately high temperature, and have certainly not been formed in contact with the fused alkaline chlorides.

*Celestine*, unlike barytes, is generally found in saliferous deposits, in which it is associated with gypsum and rock-salt, and it exists in small quantities in the gypsum of such deposits. If the gypsums are rich in organic matter, as is the case in all those in which free sulphur is found, polysulphides of calcium and strontium are formed in the interior of the rock. These polysulphides are dissolved and washed out by percolating water, and when brought in contact with the air they are decomposed, with formation of calcium sulphate, calcium carbonate, strontium sulphate, and free sulphur, and the frequent occurrence of crystals of celestine on the surface of crystals of sulphur shows that the former must have been deposited at a temperature below the melting point of the latter.

*Anhydrite* frequently alternates with gypsum, which agrees with Gorge's hypothesis, but, on the other hand, it is quite as common

in gypsum, especially in the triassic deposits in the south-east of France, where the anhydrite often passes insensibly into gypsum. It cannot be supposed that the anhydrite alternating with gypsum has been deposited from fused sodium chloride, since the gypsum begins to lose its water even below  $100^{\circ}$ . It would appear, therefore, that Gorgeu's hypothesis cannot be accepted as an explanation of the mode of formation of barytes, celestine, and anhydrite existing in veins and in saliferous deposits, although it may be of value in considering the chemical changes which accompany volcanic action.

C. H. B.

**New Locality of Chalchuite.** By W. P. BLAKE (*Amer. J. Sci.* [3], 25, 197—200).—The occurrence in New Mexico of a green turquoise, chalchuite, has already been described by the author (*Amer. J. Sci.*, 1858, 25, 227). Chalchuite also occurs in Cochise County, Arizona, in an outlying ridge of the Dragoon Mountains, now known as "Turquoise Mountain." The mineral is identical in appearance with the New Mexican variety. It is of a light green colour, with a sp. gr. of 2.71—2.82. It is peculiarly interesting archæologically. It was in general use among the Aztecs before the arrival of the Spaniards, and the author proves its identity with the *callais* or *callaina* of Pliny.

B. H. B.

**Scovillite, a new Phosphate of Didymium, Yttrium, and other rare Earths from Salisbury, Conn.** By G. J. BRUSH and S. L. PENFIELD (*Amer. J. Sci.* [3], 25, 459—463).—This mineral was discovered by J. S. Adam, occurring sparingly as an incrustation on some of the iron and manganese ores from the Scoville ore bed. The incrustation is one-sixteenth of an inch in thickness, and is frequently botryoidal or stalactitic. It is of a pink to yellowish-white colour, and presents a radiated fibrous structure.  $H. = 3.5$ . Sp. gr. 3.94—4.01. The results obtained on analysis were as follows:—

$P_2O_5$ .	$Y_2O_3 + Er_2O_3$ .	$La_2O_3 + Di_2O_3$ .	$Fe_2O_3$ .	Combined $H_2O$ .
24.94	8.51	55.17	0.25	5.88
$H_2O$ lost at $100^{\circ}$ .		$CO_2$ .	Total.	
1.49		3.59	99.83	

The presence of the carbonate is regarded as due to an admixture of lanthanite,  $(La, Di)_2(CO_3)_3, 9H_2O$ . The mineral as analysed is calculated to be a mixture of 17.04 per cent. of lanthanite, and 82.79 per cent. of the new phosphate,  $R_2(PO_4)_3, H_2O$ . Calculating the 82.79 per cent. of Scovillite up to 100 per cent., we obtain—

$P_2O_5$ .	$(YEr)_2O_3$ .	$(LaDi)_2O_3$ .	$Fe_2O_3$ .	$H_2O$ .	Total.
30.12	10.28	55.73	0.30	3.57	100.00

B. H. B.

**Analyses of Lithiophilite.** By S. L. PENFIELD (*Amer. J. Sci.* [3], 25, 176).—The author has already published analyses of triphyllite and lithiophilite from the various known localities (Abstr., 1879, 695). He now adds to these two analyses, one of lithiophilite from



Norway, Me (I), the other (II) of a variety from Branchville, Conn. The results obtained were:—

	Sp. gr.	P <sub>2</sub> O <sub>5</sub> .	FeO.	MnO.	CaO.	Li <sub>2</sub> O.
I. ...	3·398	44·40	8·60	35·98	0·78	8·50
II. ...	3·504	44·93	16·36	28·58	0·05	8·59

	Na <sub>2</sub> O.	H <sub>2</sub> O.	Gangue.	Total.
I. ....	0·14	1·19	0·12	99·71
II. ....	0·21	0·54	0·13	99·39

These analyses fully substantiate the formula Li(MnFe)PO<sub>4</sub>, already made out for the species. B. H. B.

**Determination of Alkalis in Lepidote from India.** By M. PAGE (*Chem. News*, **48**, 109—110).—The mineral examined, of a lead grey colour, was found in granite associated with a violet-red lepidote, quartz, and occasionally tinstone. The total alkalis and sodium and potassium were determined in the usual way; lithium was determined as phosphate; rubidium by fractional precipitation with platonic chloride and numerous washings with boiling water. The results per cent. are:—

K <sub>2</sub> O.	Li <sub>2</sub> O.	Na <sub>2</sub> O.	Rb <sub>2</sub> O.
8·595	1·754	0·609	0·070

D. A. L.

**Topaz from Maine, U.S.** By C. M. BRADBURY (*Chem. News*, **48**, 109).—The sample examined consisted of large colourless translucent topaz crystals; sp. gr. 3·54. An analysis yielded the following figures:—Al 27·14; Si 14·64; F 29·21; O 28·56; total, 99·55. This is very anomalous, as three-quarters and not half the oxygen, corresponding with silicon, is replaced by fluorine in ordinary topaz. Berzelius's analytical method was employed. D. A. L.

**Analyses of Franklinite Ores from New Jersey.** By P. RICKETTS (*Dingl. polyt. J.*, **248**, 523).

	I.	II.	III.	IV.
SiO <sub>2</sub> .....	11·85	11·59	8·64	10·70
ZnO.....	34·13	40·83	34·70	33·09
FeO, Fe <sub>2</sub> O <sub>3</sub> , and Fe <sub>3</sub> O <sub>4</sub>	28·48	29·94	28·34	31·05
Al <sub>2</sub> O <sub>3</sub> .....	0·58	traces	traces	traces
MnO.....	14·13	8·35	15·50	15·51
CaO.....	5·51	4·16	5·70	4·59
MgO.....	0·13	0·79	1·44	0·27
CO <sub>2</sub> ..	4·96	4·12	6·26	4·38
Cu.....	0·07	—	traces	traces
	<hr/> 99·84	<hr/> 99·78	<hr/> 100·48	<hr/> 99·59

The following composition corresponds with the latter analysis:—

Franklinite.....	51·51
Red zinc oxide .....	6·40
Rhodonite .....	11·13
Willemite .....	20·23
Manganese carbonate .....	1·24
Limestone .....	8·76
	<hr/>
	99·27

Analysis of the most important constituents gave:—

Zinkite.	Franklinite.	Willemite.
ZnO.... 95·20	ZnO.... 20·72	ZnO.... 69·97
MnO ... 3·19	MnO ... 12·72	MnO ... 1·14
	Fe <sub>3</sub> O <sub>4</sub> ... 63·90	Fe <sub>3</sub> O <sub>4</sub> ... traces
		SiO <sub>2</sub> ... 16·81
		D. B.

**Chrysocolla from Arizona.** By W. C. EUSTIS (*Chem. News*, **48**, 109).—The specimen for analysis was associated with a bluish-green variety of chrysocolla, and with much carbonate. The sample analysed was emerald-green, transparent, and pseudomorphous, with vitreous lustre. Sp. gr. 2·3; hardness, 3·5. Analysis yielded CuO, 32·22; SiO<sub>2</sub>, 34·08; H<sub>2</sub>O, 31·65; total, 98·95. These figures approximate to the formula 3CuO, 4SiO<sub>2</sub>, 13H<sub>2</sub>O, which corresponds with some specimens of chrysocolla of the constitution CuSiO<sub>3</sub>, 3H<sub>2</sub>O, in which one quarter of the copper is replaced by hydrogen; the mineral analysed may be looked upon as a copper hydrogen silicate. D. A. L.

**Rocks of the Yellowstone Park.** By W. BEAM (*Amer. J. Sci.* [3], **25**, 106).

1. *Porphyritic Obsidian*.—Colour greenish-black, semi-transparent. H. = 6. Sp. gr. = 2·4. The analysis gave—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> and Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
77·00	13·40	1·25	1·19	3·43	3·62	0·70	100·59

2. *Pebble of quartz trachyte covered with a deposit from Echinus Geyser*.—The pebble analysed was about 1·5 inches in diameter, of a light fawn colour, and contained small masses of colourless silica. The analytical results were as follows:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
77·90	14·55	0·40	trace	4·63	2·10	1·00	100·58
						B. H. B.	

**Volcanoes of Northern California, Oregon, and Washington.** By A. HAGUE and J. P. IDDIGS (*Amer. J. Sci.* [3], **26**, 222—235).—During the year 1870 the geologists attached to the Geological Exploration of the Fortieth Parallel, made a preliminary survey of the extinct volcanic cones of North California, Oregon, and Washington, but a further study was never undertaken. As the rock specimens then collected may be considered as representing the principal types

of the ejected lavas, a large number of thin sections have recently been made, and their microscopic examination has been followed up by chemical investigation.

The four great cones, Lassen's Peak, Mt. Shasta, Mt. Hood, and Mt. Ranier, which may be taken as typical of the chain, are all andesite volcanoes, with extrusions of basalt. Similar variations in mineral composition and minute details of structure are found at each of the volcanoes. All the rocks from these volcanoes may be classified under the heads of basalt, hypersthene-andesite, hornblende-andesite, and dacite.

*Hypersthene-andesite*.—These rocks are generally very porous, varying in colour from blue-black to steel-grey. They occur in all stages, from crystalline, dense forms to glassy pumice. They are generally crowded with very small porphyritic crystals, of which the felspars are the most noticeable, the iron magnesium silicates being more apparent in the light-coloured varieties. A complete chemical analysis is given (I) of a pumice from which the hypersthene was extracted. The ground-mass is an almost pure glass, and the microscope shows that the hypersthene was the first of the essential minerals to crystallise out from the original magma. The analysis of this pumice does not very materially differ from the analysis of the more compact lavas. After separating the heavier minerals from the felspar and glass, the latter were subjected to Thoulet's solution, in order to isolate the glass from the felspar. Two separations of felspar were obtained, one with sp. gr. from 2.66—2.68, and the other from 2.64—2.66. Analyses of these are given (III and IV). These probably represent the same felspar rendered impure by foreign ingredients. An analysis of the glass which forms the base of the pumice is given under V. Sp. gr. = 2.29.

	I.	II.	III.	IV.
SiO <sub>2</sub> .....	62.00	50.33	56.41	56.95
Al <sub>2</sub> O <sub>3</sub> .....	17.84	0.97	27.39	27.47
FeO .....	4.40	22.00	0.69	trace
CaO .....	5.37	1.88	9.87	9.10
MgO .....	2.64	23.29	0.09	0.02
K <sub>2</sub> O .....	1.47	—	0.36	0.48
Na <sub>2</sub> O .....	4.29	—	5.43	5.78
MnO.....	trace	0.64	—	—
TiO <sub>2</sub> .....	0.17	—	—	—
P <sub>2</sub> O <sub>5</sub> .....	0.29	—	—	—
Ignition .....	1.66	—	—	—

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Total ....	100.13	99.11	100.24	99.80
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*Dacite*.—This rock occurs near the highest point of Lassen's Peak. It is probably the most recent extrusion from the peak, and is quite unlike the rocks obtained from the other volcanoes. The specimens vary from a moderately compact rock to others of a pumice-like character. The rock is composed of quartz, mica, hornblende, and plagioclase, and is from 6—9 per cent. richer in silica than the pre-

vailing rocks of the four main cones (Analysis VI). Analyses of the felspar (VII) and of the glass (VIII) are given. The felspar is probably a mixture of andesine and oligoclase.

	V.	VI.	VII.	VIII.
SiO <sub>2</sub> .....	69.94	69.36	65.77	76.75
Al <sub>2</sub> O <sub>3</sub> .....	15.63	16.23	21.51	12.32
Fe <sub>2</sub> O <sub>3</sub> .....	—	0.88	—	—
FeO .....	1.89	1.53	trace	1.36
CaO .....	2.49	3.17	5.72	1.18
MgO .....	0.28	1.34	—	—
K <sub>2</sub> O .....	2.85	3.02	0.83	3.98
Na <sub>2</sub> O .....	3.83	4.06	5.92	3.55
Ignition .....	3.25	0.45	0.34	0.54
Total ....	100.16	100.04	100.09	99.68

The four types of rocks, basalt, hypersthene-andesite, hornblende-andesite, and dacite, exhibit four well characterised groups, but they are not sharply defined and distinct forms, as between any two in the series all possible intermediate varieties exist. B. H. B.

**Meteoric Iron from Georgia.** By C. U. SHEPARD (*Amer. J. Sci.* [3], 26, 336—338).—The mass here described was found in 1879 about 14 miles north-east of Dalton, Whitfield Co., Georgia. It weighed 117 lbs. Its shape is somewhat that of a pear. The surface is black and very little oxidised. The sp. gr. is 7.986, which is somewhat higher than is usual in meteoric iron. The analysis gave the following results:—

Fe.	Ni.	Co.	Total.
94.66	4.80	0.34	99.80

with traces of phosphorus, chromium and manganese.

B. H. B.

**Geyser Waters and Deposits.** By H. LEFFMANN (*Amer. J. Sci.* [3], 25, 104—105).—The specimens from which the following analyses were made were collected from the Yellowstone Park in 1878. Most of the geysers and hot springs are siliceous, and in most of the waters examined the silica is in the free condition. All the results are given in grains to the imperial gallon:—

1. *Pearl Geyser.*

CaSO <sub>4</sub> .	Na <sub>2</sub> SO <sub>4</sub> .	NaCl.	SiO <sub>2</sub> .	Total.
1.40	1.89	61.39	7.84	72.52

At the bottom of the bottle containing this water was a quantity of gelatinous matter, which was found on analysis to be composed of 79.1 per cent. SiO<sub>2</sub> and 4.9 H<sub>2</sub>O, together with traces of Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and CaO.

2. *Jug Spring.*

CaCO <sub>3</sub> .	Na <sub>2</sub> CO <sub>3</sub> .	Na <sub>2</sub> SO <sub>4</sub> .	NaCl.	SiO <sub>2</sub> .	Total.
0.79	49.14	2.12	31.57	14.56	98.18

3. *Opal Spring.*

NaCl.	CaSO <sub>4</sub> .	CaCl <sub>2</sub> .	SiO <sub>2</sub> .	Total.
72.18	3.22	4.06	53.76	143.22

This is not a geyser but a spring having the temperature of 90° F. The water is opalescent.

4. *Deposit from Bronze Spring.*—This occurs in convoluted layers with bronze-coloured surfaces and fawn-coloured streak, H. = 5.5. The results obtained on analysis were as follows:—

SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .	Organic matter and water.
83.1	1.2	13.6

B. H. B.

**Solid and Gaseous Constituents of Sea Water and Oceanic Deposits.** By H. TONROE and L. SCHMELCK (*Bied. Centr.*, 1883, 217—231).—These investigations were made by the Norwegian North Atlantic Expedition in 1876–78, when a tract of ocean lying between 60° and 80° N. and 12°–37° E. was examined.

*Solid Constituents.*—There is but very little variation of the sp. gr. found; a few samples, however, were much lighter, but this was due to the neighbourhood of ice, or river mouth, as the solids still bore a constant ratio to one another. As regards the percentages of chlorine, lime, magnesia, and sulphuric acid present in water taken from various depths, they remain practically constant, neither are they affected by the latitude; in those cases in which potassium has been estimated (as chloride) no variation has been found. The authors found only 0.0025 gram per 100 c.c. of organic matter, and no hydrogen sulphide. When sea water is boiled, the evaporated water being constantly replaced, all the carbonic anhydride is expelled, and a precipitate of magnesium salt free from lime is formed; but if on the contrary, the water be evaporated to say one-half, only part of the gas is driven off, and the precipitate consists of calcium carbonate and gypsum; in both cases the water becomes alkaline; further concentration causes the precipitation of gypsum and sodium chloride, the mother-liquor containing all the magnesium and potassium salts.

*Air in Sea Water.*—Jakobsen in 1871–72 found less oxygen at lower depths than at the surface.

Buchanan found the percentage of oxygen in surface water to vary with the latitude: so do the authors, obtaining 33.93 per cent. (mean) in the German Ocean, 34.94 per cent. in latitude 50–70° N., and 35.54 per cent. in latitude 70–80°.

As these results do not tally with those obtained by Bunsen, who states that the composition of the absorbed air is constant for all temperatures: experiments to elucidate the question were made, and the conclusion arrived at was, that seeing that the percentage of nitrogen was normal, there must be some unknown factor which causes the water to be supersaturated with oxygen.

When comparing the volumes of oxygen in the water collected from different depths, it was noticed that the reduction was at first very rapid, but soon became less so, and at 1000 m. the minimum was

reached, increasing slowly afterwards, being 0·4 per cent. at 3000 m. The curves representing percentages of salt and nitrogen at different depths, show that the percentage of nitrogen is inversely proportional to that of salt.

*Deposits.*—Schmelck collected 300 samples of the sea bottom, and all may be classed under the name of clay, but of this clay there are five kinds—grey, transition, biloculine, rhabdamine, and volcanic.

The grey clay covers the whole surface of the bed of the sea, but is superposed at depths of more than 1000 fathoms by biloculine; in shallow seas, as along the coast of Norway and Spitzbergen, much sand, flint, and mussel shells are found, the percentage of calcium carbonate being 9 per cent. At 500 fathoms, brown clay overlies the grey; this brown clay is distinguished from the brown biloculine which only appears at 1000 fathoms by the coarse sand present, and the paucity of Foraminifera; it is this clay which has been termed "transition." Biloculine, which is distinguished from grey clay by its colour, and from transitional by its structureless fineness and uniformity of external appearance, is rich in Foraminifera, and consequently in lime: the principal Foraminifera present being *Globigerina biloculina*, *lituola*, and *nonionina*; the minerals are microscopic grains of quartz and flakes of mica; one difference is remarkable, that whereas these particles are sharp-edged in this clay, these are all rounded in the transition clay. The green or rhabdaminic clay is found in the shallow waters which lie between Norway, Beren's Island, and Nova Zembla, and contains a large number of Foraminifera, but little calcium carbonate, much silica. Volcanic sands and dark green sandy clay is found about Jan Mayen's Land, and contains lava, tufa, felspath, angite, hornblende, magnetit and olivin. All of these deposits vary considerably in their percentage of ferrous oxide, the lighter coloured kind containing least.

E. W. P.

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## Organic Chemistry.

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**Bromine Substitution Products of Ethane and Ethylene.**  
By R. ANSCHÜTZ (*Annalen*, **221**, 133—157).—The author has carefully examined the physical properties of the bromine substitution-products of ethylene and ethane, and many of the results have already appeared in this Journal (Abstr., 1880, 98). The boiling points and specific gravities of the compounds are given in the following table:—

	b.p.	Sp. gr.	
		<i>t.</i>	$d_{4.}^{t}$
$\text{CH}_3.\text{CH}_2\text{Br}$ . . . . .	38.4°	15.0°	1.4189
$\text{CH}_3.\text{CHBr}_2$ . . . . .	110.5	21.5	2.0822
$\text{CH}_2\text{Br}.\text{CH}_2\text{Br}$ . . . .	131.6	21.5	2.1767
$\text{CHBr}_2.\text{CH}_2\text{Br}$ . . . .	187—188	21.5	2.6107
$\text{CBBr}_3.\text{CH}_2\text{Br}$ . . . . .	103.5*	21.5	2.9216
$\text{CHBr}_2.\text{CHBr}_2$ . . . .	114.0*	21.5	2.9629
$\text{CH}_2:\text{CHBr}$ . . . . .	16.0	11.0	1.5286
$\text{CBBr}_2:\text{CH}_2$ . . . . .	91.5	20.6	2.1780
$\text{CHBr}:\text{CHBr}$ . . . .	110.0	17.5	2.2714
$\text{CBBr}_2:\text{CHBr}$ . . . . .	162.5	0.0	2.6900

From these results it appears that the addition of bromine raises the boiling point and increases the sp. gr. of the derivatives of ethane and ethylene. An unsymmetrical bromine-compound has a lower boiling point and a lower sp. gr. than its symmetrical isomeride. The boiling points of the ethane derivatives are higher than those of the corresponding ethylene compounds, but the specific gravities are lower.

W. C. W.

**Nitro-derivatives of Ethylene.** By A. VILLIERS (*Compt. rend.*, 97, 258—260).—When the compound  $\text{C}_2(\text{NO}_2)_4\text{Br}_2.2\text{KHO}$  (Abstr., 1882, 815) obtained by the combination of potassium hydroxide with tetranitroethylene bromide is treated with dilute acids, it yields a yellowish oily liquid with a penetrating odour. This liquid is probably tetranitroethylene bromide. It may be heated to 100° without detonation, but is very unstable even at the ordinary temperature. The action of nitric acid on monobromomethylene bromide, and on monobromomethane yields the same product as the action of nitric acid on ethylene bromide. When this compound is treated with sodium amalgam, or with zinc in presence of dilute alkali, it is reduced with formation of ammonia, hydrobromic acid, and hydrocyanic acid. With ammonium sulphide several products are formed. If the potassium compound of tetranitroethylene bromide is mixed with ammonia and a quantity of water insufficient to dissolve it, and treated with hydrogen sulphide for a very short time, the precipitated sulphur is mixed with a compound which dissolves easily on gently warming, and is deposited in crystals on cooling. This compound forms pale-brown crystals of the composition  $\text{C}_4\text{K}_2(\text{NO}_2)_4$ . When heated gently, it decrepitates at a temperature below 100°, and is converted into a powder without change of constitution. The same molecular change takes place gradually at the ordinary temperature. At 200° the compound detonates violently, and when treated with even very dilute acids, it is completely decomposed with a violent explosion.

C. H. B.

**Derivatives of Mannite Hexylene.** By L. HENRY (*Compt. rend.*, 97, 260—263).—*Hexylene monochlorhydrin*,  $\text{C}_6\text{H}_{12}\text{Cl.OH}$ , is obtained

\* Under a pressure of 14 mm.



by the action of hypochlorous acid on hexylene or by the action of hydrochloric acid on hexylene oxide. The product of the first reaction boils at about  $170^{\circ}$ , and its sp. gr. = 1.018 at  $11^{\circ}$ . As Domac has shown, it is the  $\alpha$ -derivative, and has the constitution—



The product of the second reaction is probably the  $\beta$ -derivative, with the constitution  $\text{CHMeCl}.\text{CH}(\text{OH}).\text{CH}_2.\text{CH}_2\text{Me}$ . It is a slightly viscous colourless liquid with a peculiar odour, and a very sharp sweetish taste. It is insoluble in water, and boils without decomposition under a pressure of 761 mm.; its sp. gr. at  $11^{\circ}$  = 1.0143.

*Hexylene monobromhydrin*,  $\text{C}_6\text{H}_{12}\text{Br}.\text{OH}$ , obtained by the action of hydrobromic acid on hexylene oxide, is a colourless slightly viscous liquid, which becomes yellowish after some time. It has a penetrating odour, and a sharp taste, is insoluble in water, and boils at  $188$ — $190^{\circ}$  under a pressure of 769 mm.; its sp. gr. at  $11^{\circ}$  = 1.2959. It probably has the constitution  $\text{Me}.\text{CHBr}.\text{CHPr}(\text{OH})$ .

*Hexylene moniodhydrin*,  $\text{C}_6\text{H}_{12}\text{I}.\text{OH}$ , obtained by the action of hydriodic acid on hexylene oxide, is a colourless liquid which rapidly becomes brown on exposure to light. It is insoluble in water, and cannot be distilled.

*Hexylene acetochlorhydrin*,  $\text{C}_6\text{H}_{12}\text{Cl}.\text{AcO}$ , formed by gently heating the monochlorhydrin with acetic chloride, is a colourless liquid, insoluble in water; b. p.  $188$ — $190^{\circ}$ ; its sp. gr. at  $6^{\circ}$  = 1.04.

*Hexylene chloronitrin*,  $\text{C}_6\text{H}_{12}\text{NO}_3\text{Cl}$ , and *hexylene dinitrin*,  $\text{C}_6\text{H}_{12}(\text{NO}_3)_2$ , are formed when hexylene oxide or the monochlorhydrin is added to a cooled mixture of nitric and sulphuric acids. They are colourless combustible liquids, with a peculiar faint odour, insoluble in and heavier than water. They cannot be distilled.

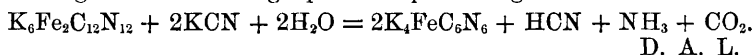
*Hexylene dichloride*, obtained as a secondary product in the preparation of the monochlorhydrin or by the action of phosphorus pentachloride on hexylene oxide, is a colourless mobile liquid, which is not altered by exposure to light. It has a faint pungent odour and a sweetish bitter taste; its sp. gr. is 1.0527 at  $11^{\circ}$ . It boils at  $162$ — $165^{\circ}$  under a pressure of 764 mm., and may be distilled over potash without undergoing alteration.

*Monochlorhexylene*,  $\text{C}_6\text{H}_{11}\text{Cl}$ , formed by the action of concentrated alcoholic potash on the dichloride,  $\text{C}_6\text{H}_{12}\text{Cl}_2$ , is a colourless mobile liquid insoluble in water, with a peculiar disagreeable odour, and a sharp taste. It is not altered by exposure to air, and boils at  $122^{\circ}$  under a pressure of 768 mm.; its sp. gr. at  $11^{\circ}$  = 0.9036; vapour-density 4.02.

*Hexylene ketone*,  $\text{C}_6\text{H}_{12}\text{O}$ , obtained by the action of sulphuric acid on monochlorhexylene, is a colourless mobile liquid with an agreeable pungent odour and very sharp taste. It is insoluble in water, and boils at  $125^{\circ}$  under a pressure of 753 mm.; its sp. gr. at  $11^{\circ}$  = 0.8343; vapour-density 3.45. The ketone is not decomposed by phosphorus pentachloride in the cold. Its constitution will depend on that of the monochlor-derivative, which has not yet been determined.

C. H. B.

**Reduction of Potassium Ferricyanide by Potassium Cyanide.** By C. L. BLOXAM (*Chem. News*, 48, 73).—The potassium cyanide employed contained but little carbonate, but on distilling it with water hydrocyanic acid and ammonia were found in the distillate, whilst the liquid in the retort contained,—besides cyanide,—potassium hydroxide, carbonate, and a little formate. When distilled with potassium ferricyanide, it yielded a distillate containing hydrocyanic acid and ammonium carbonate, the latter increasing in quantity towards the end of the reaction, whilst the residual liquid, when cool, deposited abundant crystals of potassium ferrocyanide, leaving small quantities of potassium cyanate and formate in the neutral mother-liquor. The author gives the following equation representing this reaction:—



**A Polymeride of Trichloroacetonitril.** By A. WEDDIGE (*J. pr. Chem.* [2], 28, 188—189).—By heating ethyl paracyancarbonate (this Journal, 1874, 448) with phosphoric chloride, a thick yellowish-brown oil is obtained, which from its reactions appears to be paracyancarbonic chloride. By further heating this oil with phosphoric chloride in sealed tubes at 155—160°, a substance is obtained having the composition of trichloroacetonitril, but different properties. It crystallises in large plates or prisms, melts at 91—92°, is insoluble in water, readily soluble in alcohol, ether, and benzene. By boiling with alcoholic ammonia, it is converted into a compound of the formula  $\text{C}_6\text{H}_5\text{Cl}_7\text{H}_4$  or  $\text{C}_6\text{H}_3\text{Cl}_7[\text{NH}_2]_2$ , crystallising well and melting at 165°. A chlorinated product of feeble basic properties is obtained by heating in sealed tubes with aqueous or alcoholic ammonia.

A. J. G.

**Action of Aldehyde on Propyl Glycol.** By A. DE GRAMONT (*Compt. rend.*, 97, 173).—Equal parts of aldehyde and isopropyl glycol are heated together in sealed tubes at about 160° for two days, and the product is distilled. That portion which boils between 75° and 110° is dried over calcium chloride and fractionated. In this way a colourless, highly refractive liquid of ethereal odour is obtained. It boils at about 93°, and its sp. gr. is lower than that of water, in which it is only slightly soluble. The analysis of the liquid and the determination of its vapour-density did not give satisfactory results, but in all probability it is propyleneacetal, formed by the union of aldehyde and isopropyl glycol with elimination of water. In contact with water it yields aldehyde and isopropyl glycol.

Isopropylene oxide has no action on aldehyde in sealed tubes below 140°, but above this temperature decomposition takes place with formation of volatile and carbonaceous products.

C. H. B.

**Constitution of Natural Fats.** By J. A. WANKLYN and W. FOX (*Chem. News*, 48, 49).—The authors suggest that some fats, which do not yield glycerol on saponification, are in all probability ethers of isoglycerol. Isoglycerol,  $\text{CH}_2\text{Me.C}(\text{OH})_3$ , exists in its ethers, cannot be isolated, and ought to be resolved into  $\text{CH}_2\text{Me.COOH} + \text{H}_2\text{O}$ .

D. A. L.

**New Derivatives of Mannitol.** By A. GEUTHER (*Annalen*, **221**, 59—60).—The author noticed that a white flocculent precipitate was gradually separated from a perfectly clear sample of butyric acid; it was filtered off, purified from the adhering acid by heating to  $170^{\circ}$ , and dissolved in water. On evaporating the aqueous solution, a gummy mass of the composition  $C_{12}H_{18}O_7$  was obtained. As the process of lactic and butyric fermentation is always accompanied by a partial conversion of the sugar into mannitol, then this substance is probably an anhydride of mannitol,  $C_{12}H_{18}O_7 = 2C_6H_{14}O_6 - 5OH_2$ , and is thus a homologue of mannitan,  $C_6H_{12}O_5$ , and mannide,  $C_6H_{10}O_4$ .  
V. H. V.

**Relation between the Solubility and Rotation of Milk-sugar, and Rate of Transition of its Birotation into Normal Rotation.** By F. URECH (*Ber.*, **16**, 2270—2271).—When finely divided milk-sugar is agitated with a quantity of water insufficient to dissolve it, a saturated solution is obtained, which exhibits birotation; but the solution gradually takes up more milk-sugar as the transition from birotation to normal rotation takes place, showing that the solubility is thereby increased. When two saturated solutions are prepared at temperatures differing by about  $20^{\circ}$ , and the warmer solution is allowed to cool down to the temperature of the other, it will still contain much more milk-sugar than the solution prepared at the lower temperature, the greater solubility at the higher temperature being due not only to the difference of temperature, but also to the more rapid conversion at a raised temperature of the birotatory sugar into the much more readily soluble sugar of normal rotation. The transition from birotation to normal rotation takes place slowly at atmospheric temperature, so that the rate of change can readily be measured by the polariscope and formulated in the same way as the rate of inversion of saccharose.  
A. K. M.

**Starch and its Transformations under the Influence of Acids.** By F. SALOMON (*J. pr. Chem.* [2], **28**, 82—154).—The principal conclusions drawn by the author from this lengthy investigation are as follows:—The transformation of starch by dilute sulphuric acid cannot be considered as a splitting up of the molecule into dextrin and dextrose, as assumed by Musculus. The products of the action of sulphuric acid on starch are soluble starch, dextrin, and dextrose; the course of the reaction being that the complex starch molecule is first converted into the more simple soluble starch, and next into the still more simple dextrin, the hydrolysis of the latter into dextrose commencing almost simultaneously. The rate of the conversion is proportional to the quantity of sulphuric acid present. The transformation of starch by organic acids (oxalic, tartaric, and citric acids) proceeds in the same manner as with inorganic acids, but the action is less vigorous.

Soluble starch, if pure, gives a deep blue coloration with iodine, but if it is contaminated with dextrin, a reddish-violet coloration is obtained; it does not reduce Fehling's solution, and has the specific rotary power  $[\alpha]_D = 211.5^{\circ}$  (comp. O'Sullivan, *Trans.*, 1879, 772). There is only evidence for the existence of a single dextrin; it gives

a brownish-red coloration with iodine, does not reduce Fehling's solution, and has the specific rotary power  $[\alpha]_D = 216.5^\circ$ .

A. J. G.

**Preparation of Isobutyraldehyde free from Acetone.** By W. FOSSEK (*Monatsh. Chem.*, **4**, 660—662).—The author's method is based on the property of the crystalline trimolecular modification of isobutyraldehyde to change into the ordinary liquid aldehyde, under the influence of strong sulphuric acid at the heat of the water-bath. The crude isobutyraldehyde was first partly purified by heating it, as previously described by the author (Abstr., 1882, 161), with a strong solution of sodium acetate at  $150^\circ$ . It was then polymerised by mixing it with strong sulphuric acid (1 g. acid to 100 g. aldehyde), or with hydrochloric acid, the formation of crystals being accelerated by cooling. These crystals were drained on a filter, washed with water, dried between filter-paper, and preserved for use. To convert them, when required, into liquid isobutyraldehyde, they are fused on the water-bath, mixed with a few drops of strong sulphuric acid, and heated on the water-bath in a reflux apparatus, whereby, after about an hour's boiling, the whole of the polymeride is converted into liquid isobutyraldehyde, boiling constantly at  $63^\circ$  (bar. 741 mm. at  $0^\circ$ ) and having a density of 0.8057 at  $0^\circ$  and 0.7898 at  $20^\circ$ , referred to water at the same temperatures. Its vapour, when inhaled, produces nausea and headache.

H. W.

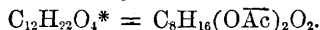
**A Derivative of Isobutyraldehyde analogous to Hydrobenzoin.** By W. FOSSEK (*Monatsh. Chem.*, **4**, 663—678).—The author has already shown (Abstr., 1883, 1278) that when the products of the action of aqueous potash on isobutyraldehyde are distilled with steam, a thick yellow oil remains, holding in solution two isomeric crystalline bodies,  $C_8H_{16}O_2$ , resembling one another in their chemical reactions (which are those of the pinacones), but differing in crystalline form, solubility, and melting point, the more abundant of the two crystallising in plates, being moderately soluble in water, and melting at  $151^\circ$ , whereas the other crystallises in groups of needles, dissolves but very sparingly in water, and melts at  $91^\circ$ . The former was extracted from the oil by agitation with hot water; the latter separated out on adding light petroleum. This higher-melting body could not at first be satisfactorily examined, on account of the very small quantity in which it was obtained; but the author has since found that it may be prepared much more readily by acting on isobutyraldehyde with alcoholic instead of aqueous potash, forming indeed the chief product of the reaction, which likewise yields isobutyric acid and a hydroxy-acid to be described further on.

The crystalline body melting at  $91^\circ$  is found by analysis to have the composition  $C_8H_{16}O_2$ , and its reactions show that it consists of di-isopropyl-glycol,  $CHPr^{\beta}(OH).CHPr^{\beta}(OH)$ . It dissolves readily in alcohol and ether, somewhat less readily in water, and separates on quick evaporation of its aqueous solution, as a supernatant oil, which, on contact with a solid body, suddenly solidifies to a cake. By very slow evaporation, however, at temperatures near  $0^\circ$ , it may be obtained in monoclinic crystals having the axial ratio  $a : b : c =$

0.8223 : 1 : 1.9086, and the angle  $ac = 97^\circ 30'$ . Observed faces,  $\infty P\infty$ ,  $0P$ ,  $+P$ ,  $-P$ . The crystals are flattened by predominance of  $\infty P\infty$ . Twins occur united by this face. The vapour-density of the compound is by experiment 67.71—70.03; calc. 73.00.

By oxidation with nitric acid, the glycol yields isobutyric and oxalic acids; with potassium permanganate in neutral solution, the isobutyric acid formed in the first instance is further oxidised to acetic and carbonic acids.

Di-isopropyl glycol boiled for about two hours with a slight excess of acetic chloride, yields an oily diacetate,



Treated with an equal weight of a mixture in equal parts of strong sulphuric acid and water, it dissolves in a few minutes, especially if the mixture be heated in a reflux apparatus, and there rises to the surface an oil having a camphorous odour; and on separating this oil after boiling with ether for half an hour, washing the ethereal solution with aqueous sodium carbonate, evaporating off the ether, and drying the remaining liquid with calcium chloride, a residue is obtained which may be separated by fractional distillation into two liquids, the smaller in quantity smelling like camphor and boiling at  $120$ — $122^\circ$ , whilst the other, which is viscid and nearly colourless, distils at  $260$ — $262^\circ$ . Both these liquids have the composition  $C_8H_{16}O$ . They are not aldehydes, and therefore the oxygen contained in them is probably related to the other elements in the same manner as in oxides or in ketones.

The glycol heated for 6—8 hours in a sealed tube at  $140^\circ$  with ten times its weight of fuming hydriodic acid, is converted into an iodide which, when decomposed by alcoholic potash, yields an *octylene*,  $C_8H_{16}$ , in the form of a colourless mobile liquid, which has a strong odour of petroleum, distils for the most part at  $116$ — $120^\circ$ , and unites readily with bromine, forming a very unstable addition-product. The mode of its formation from di-isopropyl glycol shows that it must be represented by the formula  $CHPr^{\beta} : CHPr^{\beta}$ .

The action of alcoholic potash on isobutyraldehyde gives rise also to isobutyric acid and a small quantity of a hydroxy-acid,  $C_8H_{16}O_3$ , which forms a white anhydrous crystalline powder, sparingly soluble in water and in ether, easily in alcohol; does not volatilise with steam; melts at  $92^\circ$ , and distils at a high temperature: its silver salt is amorphous, and melts at  $120^\circ$ . The constitution of this acid has not yet been made out.

The formation of di-isopropyl glycol and isobutyric acid from isobutyraldehyde is represented by the equation—

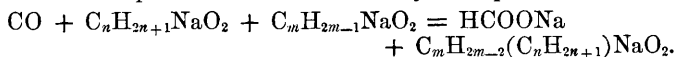


H. W.

**Action of Carbonic Oxide on Mixtures of Sodium Alcohols and Sodium Salts of Organic Acids.** By M. SCHROEDER (*Annalen*, 221, 34—55).—The researches of Geuther and Froelich, Looss and Poetsch (*Abstr.*, 1883, 729) on the action of carbonic oxide

\* In the original paper the formula is printed  $C_{16}H_{22}O_4$ , which does not agree either with the rational formula or with the analysis ( $C = 62.62$ ,  $H = 9.52$ ).—H. W.

on sodium alcoholates, have proved that a small quantity of the sodium salt of the corresponding carboxyl acid is formed. But in the presence of a considerable quantity of this latter salt, sodium formate is obtained, together with the sodium salts of homologous and isologous acids. The first phase of this reaction may be expressed as follows:—



The author has studied the same reaction in the case of sodium phenates and the sodium salts of organic acids belonging to various series. When carbonic oxide is passed into a heated mixture of sodium phenylate and acetate, a hydrogen-atom of the acetic acid is not replaced by phenyl with formation of phenylacetic acid, but sodium salicylate is obtained in small quantity. This result is probably due to the presence of sodium carbonate in the alcoholate which yields the carbonic anhydride. The supposition the author confirms experimentally. Similarly in the action of carbonic oxide on sodium ethylate and benzoate, the hydrogen of the benzoic acid is not replaced by an ethyl-group. Conversely, when sodium phenylacetate is substituted for sodium benzoate, the sodium salts of phenylethylacetic,  $\text{CH}_2\text{EtPh.COOH}$ , and ethenylbutenylphenylacetic,  $\text{CPhC}_2\text{H}_3.\text{C}_2\text{H}_2\text{Et.COOH}$ , acids are formed; in this respect phenylacetic behaves precisely as acetic acid.

By the action of carbonic oxide on sodium ethylate and cinnamate, the sodium salts of diethylcinnamic acid,  $\text{C}_9\text{H}_8\text{Et}_2\text{O}_2$ , were formed in one set of experiments, when the mixture was more completely exposed to the action of the gas. In another set, the sodium salt of dibutyl cinnamic acid was obtained, derived doubtless from the diethylcinnamic acid by the replacement in each ethyl-group of a hydrogen-atom by another ethyl-group.

Experiments on the action of carbonic oxide on mixtures of sodium ethylate and potassium oxalate or sodium succinate led to negative results.

V. H. V.

### Behaviour of Chromium, Iron, and Aluminium Acetates.

By B. REINITZER (*Chem. News*, **48**, 114).—When a solution of chromium sulphate or chloride is boiled with excess of sodium acetate, no precipitate is formed, but if the boiling is conducted for a short time only, the solution becomes violet on cooling. The solution thus prepared behaves in the following manner in the cold:—Caustic alkalis and barium hydroxide change the colour at first to olive-green and then to emerald-green, and in 12 hours the liquid sets to a green jelly. Ammonia produces no immediate effect, but in 48 hours a violet jelly is formed; ammonium sulphide and carbonate act in a similar manner after several days. When the violet chromium acetate solution is boiled with any of these reagents, or with an alkaline or barium carbonate, a precipitate is produced, immediately or otherwise, according to the strength and quantity of the reagent added. Sodium phosphate does not precipitate the solution. This non-precipitating property of chromium acetate extends to iron and alumina in solution, for neither by boiling nor by treatment with the above-mentioned reagents can certain quantities of ferric oxide and alumina be de-

ected in the presence of chromium acetate. The quantity of these oxides thus retained is limited if the ferric oxide and alumina are present previous to boiling with sodium acetate; if, however, these substances are added subsequent to sodium acetate treatment, large quantities of iron and alumina can be dissolved. Ammonium sulphide makes an exception in the case of iron, for it precipitates it slowly but completely. If the chromium solution and sodium acetate are simply mixed in the cold, at first the chromium can be precipitated by the reagents referred to above; after a day, however, the solution acquires the solvent properties it would have done by boiling.

D. A. L.

**Composition of Cocoa-butter.** By M. C. TRAUB (*Arch. Pharm.* [3], 21, 19—23).—Kingzett has stated (*Trans.*, 1878, 38) that this butter contains two new fatty acids, the one apparently an isomeride of lauric acid, the other, called theobromic acid (m. p. 72·8°), and having the formula  $C_{64}H_{128}O_2$ . The anomalous melting point of such an acid led the author to make an investigation of cocoa-butter. By a process of fractional precipitation with magnesium acetate after saponification, an acid was obtained from the first portion of the precipitate, which was not further resolved by precipitation, and after recrystallising from absolute alcohol was proved to be arachic acid ( $C_{20}H_{40}O_2$ ). Fractional distillation under diminished pressure (100 mm.) confirmed the results obtained by fractional precipitation. In addition to arachic acid, oleic, lauric, palmitic, and stearic acids were found, but no acid isomeric with lauric acid. The author, therefore, cannot confirm the statement that cocoa-butter contains two new fatty acids, and maintains that its physical properties are due to the relative proportions of arachic, oleic, lauric, palmitic, and stearic acids, which are present.

W. R. D.

**Carbonyl Iodide,  $COI_2$ .** By S. P. COWARDINS (*Chem. News*, 48, 97).—Several experiments were made with a view to prepare this substance, but without success. Proportional parts of dry carbonic oxide and iodine in a flask were exposed to direct sunlight. Carbonic oxide and iodine vapour were passed through a tube surrounded by ice and salt. Carbonic oxide was passed through heated arsenic pentiodide, and then through the cooled tube, also over red-hot lead iodide. Phosgene gas was passed over potassium iodide and into condensing tubes.

D. A. L.

**Action of Phosphorus Pentachloride on Succinic Chloride.** By E. KAUDER (*J. pr. Chem.* [2], 28, 191—192).—By heating one part of succinic chloride with three parts phosphorus pentachloride in sealed tubes at 230°, there was obtained, not as was expected the chloride  $C_2H_4(CCl_3)_2$ , but a colourless liquid of sp. gr. 1·694, boiling at 199—215°, solidifying in large colourless plates at low temperatures, and having the composition  $C_4Cl_6O$ . If this is heated with sulphuric acid, it is decomposed into a substance of the formula  $C_4Cl_2O_3$ , possibly dichloromaleic anhydride,  $C_2Cl_2:(CO)_2:O$ . It forms a white mass, sparingly soluble in water, melts at 119·5°, and sublimes in white plates.

A. J. G.

**Tetric Acid and its Homologues.** By W. PAWLOW (*Compt. rend.*, **97**, 99—102).—Ethylic methylmonobromacetoacetate is slowly decomposed at ordinary temperatures and more rapidly when heated, yielding monobromomethane and the *tetric acid* described by Demarçay. This acid has the composition  $C_8H_6O_3$ , and not  $C_{12}H_{14}O_7$ , as stated by Demarçay. Ethylic isobutyl-monobromacetoacetate is decomposed in a similar manner when heated, and yields the *heptic acid* also described by Demarçay. This acid has the composition  $C_8H_{12}O_3$ , and not with Demarçay's formula  $3(C_7H_{10}O_2), H_2O$ , which requires carbon 63.63 per cent., hydrogen 8.08 per cent. The formation of these acids by simple evolution of monobromomethane indicates that they are unsaturated compounds, and tetric acid is found to combine readily with two atoms of bromine. This fact, together with its mode of formation, shows that tetric acid has the formula  $MeCO.C(COOH):CH_2$ , and is in fact *acetoacrylic acid*, the general formula of its homologues being  $MeCO.C(COOH):C_nH_{2n}$ . Its formation is expressed by the equation  $MeCO.CBrMe.COOC_2H_5 - C_2H_5Br = MeCO.C(COOH):CH_2$ . Ethyl monobromacetoacetate,  $MeCO.CHBr.COOC_2H_5$ , undergoes no similar decomposition. C. H. B.

**Carboxytartronic Acid. The Constitution of Benzene.** By A. KÉKULÉ (*Annalen*, **221**, 230—260).—After referring to the researches of Gruber (*Wien. Acad. Ber.*, 1879; *Ber.*, **12**, 514), Barth (*Wien. Acad. Ber.*, 1880; *Wiener Monatshefte*, **1**, 869), and Werzig (*Wien. Acad. Ber.*, 1882; *Wiener Monatshefte*, **3**, 825), on carboxytartronic acid, and their bearing on the constitution of benzene, the author describes experiments proving that the so-called carboxytartronic acid is a dihydroxytartaric or tetrahydroxysuccinic acid. A mixture of racemic and inactive tartaric acid is formed by the action of zinc and hydrochloric acid on sodium carboxytartronate; and carboxytartronic acid is produced as an intermediate product by the spontaneous decomposition of nitrotartaric acid.

The nitrotartaric acid is prepared by adding sulphuric acid to a solution of tartaric acid in  $4\frac{1}{2}$  times its weight of fuming nitric acid. The crystalline mass is drained by means of a filter-pump, and brought in small quantities at a time into a mixture of ice and ether. After washing with ice-cold water, the ethereal solution is evaporated in a vacuum. A solution of nitrous acid in alcohol is added to an ethereal solution of nitrotartaric acid, and after two or three days the liquid is shaken with ice-cold water. On the addition of sodium carbonate to the aqueous solution, sodium carboxytartronate is at once precipitated. The sodium salt is decomposed by water at  $60^\circ$ , with the formation of carbonic anhydride and sodium tartronate.

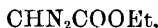
These experiments show that "sodium carboxytartronate" does not possess the constitution generally ascribed to it, and that carboxytartronic acid is closely related to tartaric acid. The exact composition of the sodium salt has not yet been ascertained, as it loses first water, and then water and carbonic acid on drying; but it is probably  $C_4Na_2O_6 + 4H_2O$ . Since this compound does not contain three carbon atoms directly united to each other, its formation from pyrocatechol



is no argument against the author's hypotheses on the constitution of benzene. W. C. W.

**Isonitroso-acids.** By A. FÜRTH (*Ber.*, **16**, 2180—2182).—Of the isonitroso-derivatives of the acids of the acetic series, only three are at present known, viz., isonitroso-propionic, -butyric, and  $\gamma$ -valeric acids. The author, following the process proposed by Wlëugel, has obtained, by the action of nitrous acid on ethylpropylacetoacetate,  *$\alpha$ -isonitroso-valeric acid*,  $\text{CH}_2\text{Me}.\text{CH}_2.\text{C}(\text{N.OH}).\text{COOH}$ . This acid crystallises in needles which melt at  $143^\circ$  with complete decomposition; it is soluble in alcohol and benzene, sparingly soluble in water; its silver salt forms a white precipitate. By the action of hydroxylamine hydrochloride on ortho- and para-aldehydo-salicylic acid, the author has obtained the ortho- and para-aldoximesalicylic acids,  $\text{COOH}.\text{C}_6\text{H}_3(\text{OH}).\text{CH}(\text{NOH})$ . Both acids crystallise in small golden needles. The former melts at  $193^\circ$ , the latter at  $179^\circ$ , and is more sparingly soluble than its isomeride. V. H. V.

**Action of Nitrous Acid on Ethyl-glycocine Hydrochloride.** By T. CURTIUS (*Ber.*, **16**, 2230—2231).—When a concentrated aqueous solution of the hydrochloride of the ethylic ether of glycocine is treated with sodium nitrite, a yellow oil is precipitated and can be extracted with ether. To purify it, it is treated with baryta-water, steam-distilled, dried over calcium chloride, and heated at  $95^\circ$  on a water-bath. It is a neutral liquid of golden-yellow colour and of powerful characteristic odour, miscible in all proportions with ether and alcohol, but almost insoluble in water. It volatilises on exposure to air, and when heated to about  $110^\circ$  is decomposed with violence and with great evolution of heat. It shows great stability in the presence of alkalis, but in contact with acids, water, or alcohol, it gives off nitrogen in nearly theoretical amount. With cold concentrated hydrochloric acid, the decomposition takes place with explosive violence, ethyl chloracetate being formed. On boiling it with water, the products are ethylic glycollate, glycollic acid, alcohol, and nitrogen, whilst with alcohol, ethylic ethylglycollate is produced. These reactions would indicate the body to be ethylic diazoacetate,  $\text{CH}_2(\text{N}_2\text{OH}).\text{COOEt}$ , but analysis shows that its formula is—



that is, ethylic diazoacetate minus the elements of a molecule of water.

The author is continuing his experiments in the hopes of obtaining diazo- and diazo-amido-derivatives of the fatty acids. A. K. M.

**Chemistry of Asparagine.** By B. SCHULZE (*Landw. Versuchs.-Stat.*, **29**, 233—240).—Having occasion to obtain rather large quantities of aspartic acid from asparagine, the author made several experiments to ascertain which was the cheapest and best decomposing agent to use. Schlösing's apparatus was used for determining the amount of asparagine converted into ammonium aspartate, and it was found that milk of lime had no action in the cold on asparagine until after 24 hours' standing.

Heated with water alone, at the ordinary pressure, asparagine is but very slowly decomposed; after 12 hours' boiling only 2 per cent. of the nitrogen was converted into ammonium salt. Under higher pressure the amount decomposed is much greater, and increases slowly with increase of pressure.

The effect of boiling with lime-water or baryta was much more rapid; when a large excess of baryta was used, one hour was sufficient for the complete conversion into aspartic acid; but if the boiling be continued some hours longer, a further separation of ammonia takes place, malic acid being formed.

Boiling with dilute sulphuric acid in slight excess also effects the complete conversion of asparagine into ammonium aspartate.

J. K. C.

**Metaisopropylmethylbenzene.** By H. E. ARMSTRONG and A. K. MILLER (*Ber.* 16, 2748—2750).—According to Kelbe (*Annalen*, 210, 30) metaisocymene yields at least two monosulphonic acids, the second of which, the  $\beta$ -acid, he did not thoroughly investigate, but he described the barium salt as being very readily soluble in water, and as crystallising from a concentrated syrupy solution in small lustrous scales of the composition  $(C_{10}H_{13}SO_3)_2Ba + H_2O$ . The authors, who give a full description of the method by which they prepare pure metaisocymene, also find that this hydrocarbon yields two sulphonic acids, which they separate by means of the barium salts, but Kelbe's description is entirely inapplicable to the more soluble modification. Although very soluble, it crystallises very readily in long thin prisms of the composition  $(C_{10}H_{13}SO_3)_2Ba + 9H_2O$ . The calcium salt,  $(C_{10}H_{13}SO_3)_2Ca + 5\frac{1}{2}H_2O$ , is very similar in appearance to the barium salt. The potassium salt,  $C_{10}H_{13}SO_3K + 2\frac{1}{2}H_2O$ , crystallises in long well-formed prisms.

A. K. M.

**Contributions to our Knowledge of Camphor.** By H. E. ARMSTRONG and A. K. MILLER (*Ber.*, 16, 2255—2261).—By the action of zinc chloride on camphor, Fittig, Köbrich, and Jilke (*Annalen*, 145, 129) obtained a hydrocarbon,  $C_{10}H_{14}$ , which they regarded as most probably identical with ordinary cymene, together with much toluene, xylene, pseudocumene, and *laurene*, the last-mentioned being, according to their analysis, a hydrocarbon of the formula  $C_{11}H_{16}$ . By the same reaction Montgolfier (*Ann. Chim. Phys.*, 1878 [5], 14, 87) obtained what he thought to be cymene and an isomeric hydrocarbon boiling at about  $195^\circ$ , from which he prepared a dibromo-derivative melting at  $199^\circ$ ; this isomeric hydrocarbon he assumed to be Jannasch's tetramethylbenzene (1 : 2 : 3 : 5), and regarded it as identical with Fittig's *laurene*. From the fraction  $173$ — $176^\circ$ , supposed to be cymene, Fittig, Köbrich, and Jilke prepared a sulphonic acid, the barium salt of which contained 10.13 per cent. water, whereas ordinary barium cymenesulphonate contains 8.75 per cent. It would seem that Montgolfier prepared the same salt (with 10.74 per cent. water) from the crude distillate boiling at about  $195^\circ$ . Fittig's fraction boiling at  $188^\circ$  ( $C_{11}H_{16}$ ), was assumed to be a dimethylpropylbenzene, as it yielded a tribromo-derivative melting at

125°, and on oxidation gave monobasic lauroxylic acid,  $C_9H_{10}O_2$ , melting at 155°

The authors heat camphor with twice its weight of zinc chloride at a moderate temperature, until a homogeneous mixture is obtained, and then distil at as low a temperature as possible. The crude distillate is extracted with sodium hydroxide solution, then steam-distilled, and the distillate is agitated with dilute sulphuric acid (4 vols. acid to 1 vol. water) to remove the unattacked camphor, and again steam-distilled. On passing steam into the retort, a second distillate is obtained, consisting of camphorone,  $C_9H_{14}O$ , and camphor mixed with some hydrocarbon, which can be separated by means of sulphuric acid of the above strength, in which the camphorone is soluble; a residue of zinc chloride mixed with a black carbonaceous mass remains in the retort. The above-mentioned alkaline extract yields pure carvacrol on addition of an acid.

When the mixture of hydrocarbons remaining after treatment of the crude distillate with dilute sulphuric acid, is heated with sulphuric acid, a considerable amount of a saturated hydrocarbon,  $C_{10}H_{20}$ , remains undissolved, whilst the sulphuric acid solution contains principally benzene hydrocarbons of the formula  $C_{10}H_{14}$ , only a very small amount of lower and higher homologues being formed, together with a hydrocarbon which has not yet been isolated, and which is carbonised by the action of heat on the dilute acid solution. The chief constituents of the hydrocarbon mixture are a *methylpropylbenzene*, a *dimethylethylbenzene*, and a *tetramethylbenzene*; the presence of ordinary cymene has as yet not been detected.\* The sulphonic acid of the first-mentioned hydrocarbon yields a very sparingly soluble anhydrous barium salt, a sodium salt containing 1 mol.  $H_2O$ , and an anhydrous potassium salt, the last two crystallising in large lustrous plates. The hydrocarbon boils at 176°, is oxidised by dilute nitric acid to metatoluic acid, and is identical with the metaisopropylmethylbenzene discovered by Kelbe in rosin spirit. The dimethylethylbenzene (b. p. 189°) is probably identical with Fittig's laurene; it yields paraxylic acid on oxidation, and must therefore have the constitution  $[Me : Me : Et = 1 : 2 : 4]$ . It yields two isomeric sulphonic acids. From the chief product there may be obtained a barium salt crystallising with  $4H_2O$ , and a magnesium salt containing about 25 per cent. water, magnesium cymenesulphonate containing 16.6 per cent. The tetramethylbenzene is identical with Jannasch's isodurene, and yields a dibromo-derivative melting at 209°, as stated by Jacobsen.

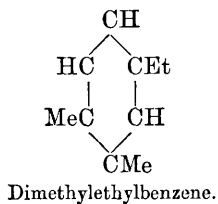
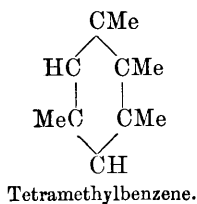
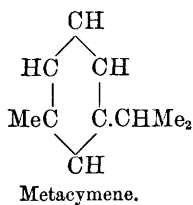
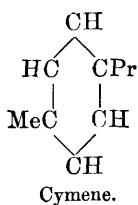
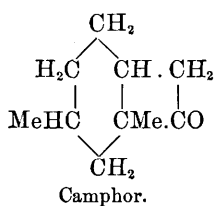
The chief products of the action of iodine on camphor are carvacrol, and the saturated hydrocarbon,  $C_{10}H_{20}$ . Dimethylethylbenzene and tetramethylbenzene are also formed, but no cymene or metacymene.

Ordinary cymene appears to be the only benzene hydrocarbon which is formed by the action of phosphoric anhydride on camphor, and is also the chief product of the action of phosphorous pentasulphide, but in the latter case a considerable amount of metaisopropyl-

\* Subsequent investigation has shown that no cymene is present.—H. E. A.

methylbenzene, and a small quantity of tetramethylbenzene are also obtained together with traces of higher and lower homologues, and a small percentage of the hydrocarbon  $C_{10}H_{20}$ . The hydrocarbon which carbonises when its sulphuric acid solution is heated (see above) is also formed by the action of phosphorus compounds and of iodine on camphor.

The formation of these different hydrocarbons from camphor cannot well be represented by Kekulé's formula, but can be to some extent accounted for by the assumption of the following formula, which is a slight modification of that previously suggested by Armstrong (*Ber.*, **11**, 1698; **12**, 1756).



A. K. M.

**Artificial Formation of Thiophene.** By V. MEYER and T. SANDMEYER (*Ber.*, **16**, 2176).—If ethylene or acetylene is passed through boiling sulphur large quantities of carbon, hydrogen sulphide, and carbon bisulphide are formed. The last contains a small quantity of an oil which resembles thiophene in all its properties, giving the indophenine reaction with isatin and sulphuric acid, and dye-stuffs with benzoyl cyanide and sulphuric acid, and with phenylglyoxylic and metazophenylglyoxylic acids.

V. H. V.

**The Thiophene Group.** By V. MEYER and H. KREIS (*Ber.*, **16**, 2172—2176).—One of the authors has recently isolated and described thiophene,  $C_4H_4S$  (*Abstr.*, 1883, p. 1091), a substance obtained from coal-tar benzene; in the present communication some of its derivatives are described.

*Tetrabromothiophene*,  $C_4Br_4S$ , is formed by the action of bromine in excess on the residue left in the course of the fractional distillation of dibromothiophene. This substance crystallises in white glistening needles melting at  $112^\circ$ , and boiling at  $26^\circ$ .

*Thiophenesulphonic acid*,  $C_4H_3S \cdot SO_3H$ , is obtained as a deliquescent crystalline mass, of strongly acid reaction, and yielding thiophene on dry distillation. The corresponding *acid chloride*,  $C_4H_3S \cdot SO_2Cl$ , is a heavy golden oil, converted by trituration with ammonium carbonate

into *thiophenesulphamide*,  $C_4H_3S.SO_2NH_2$ , which forms delicate white crystals melting at  $141^\circ$ .

*Thiophenenitril*,  $C_4H_3S.CN$ , obtained by the distillation of potassium cyanide and thiophenesulphonates, is an oil boiling at  $190^\circ$ , and smelling like bitter almonds; it is readily transformed into the *carboxylic acid*,  $C_4H_3S.COOH$ , on boiling with alkalis. Thiophenic acid resembles benzoic acid in appearance, smell, and manner of sublimation; it is very volatile in vapour of steam, melts at  $118^\circ$ , and boils at  $258^\circ$ . Its calcium salt forms spear-shaped crystals, its silver salt a precipitate, sparingly soluble when dried.

The authors briefly note the presence of a sulphur compound boiling at  $110^\circ$  in the purest toluene of commerce; they are now engaged in investigating it, and the dye-stuffs derived from it, as also those from thiophene. V. H. V.

### Separation of Aniline, Paratoluidine, and Orthotoluidine.

By LEWY (*Dingl. polyt. J.*, **248**, 260).—By decomposing the hydrochlorides of the bases with sodium phosphate, Lewy obtains the sparingly soluble phosphates of aniline and paratoluidine besides free orthotoluidine and readily soluble basic orthotoluidine phosphate. By warming the mixture after the decomposition is completed, it is possible to dissolve the first-named salts; the resulting supernatant oily layer of orthotoluidine is then decanted, and the aniline and paratoluidine salts are allowed to crystallise out. The mother-liquor contains the basic orthotoluidine phosphate. By liberating the bases with sodium hydroxide, the sodium phosphate originally used may be recovered. D. B.

**Meta-isocymidine.** By W. KELBE and C. WARTH (*Annalen*, **221**, 157—178).—*Nitrometa-isocymene*,  $C_{10}H_{13}NO_2$ , prepared by the action of strong nitric acid on meta-isocymene (*Abstr.*, 1880, 878) is decomposed by boiling, but may be distilled in a current of steam. By the prolonged action of dilute nitric acid (1 of acid to 4 of water), it is converted into *nitrotoluic acid*,  $C_6H_3Me(NO_2).COOH(\alpha)$ , which is not identical with either of the nitrotoluic acids described by Jacobsen (*Ber.*, **14**, 2347), and must consequently have the formula  $C_6H_2Me(NO_2)H.COOH(\gamma)$  or  $C_6HMe(NO_2)H_2.COOH(\delta)$ . This acid is deposited from an alcoholic solution in glistening needles (m. p.  $214^\circ$ ). The *barium* salt crystallises in silky needles, freely soluble in alcohol and in water.

*Meta-isocymidine*,  $C_{10}H_{13}NH_2$ , obtained by reducing nitro-isocymene with tin and hydrochloric acid, is purified by conversion into the benzoic-derivative,  $NH\bar{B}z.C_{10}H_{13}$ . This compound crystallises in needles melting at  $165^\circ$ , soluble in alcohol. It is decomposed by alcoholic potash at  $180^\circ$ , yielding meta-isocymidine, a strongly refractive liquid boiling at  $232^\circ$ , freely soluble in alcohol, ether, benzene, and light petroleum. The platinochloride of meta-isocymidine is unstable. The *sulphate*,  $(C_{10}H_{13}.NH_2)_2H_2SO_4$  forms thin plates, sparingly soluble in water and alcohol. The aqueous solution is decomposed by boiling. The *oxalate*,  $C_{10}H_{13}.NH_2.H_2C_2O_4$ , is sparingly soluble in water and alcohol.

Acetic chloride acts readily on dry cymidine, forming *acetometaisocymidide*,  $\text{NHAc.C}_{10}\text{H}_{13}$ , which crystallises in plates melting at  $118^\circ$ . By the action of strong nitric acid on benzoic isocymidide, the nitro-compound  $\text{NHBz.C}_{10}\text{H}_{12}.\text{NO}_2$  is produced. It is deposited from an alcoholic solution in yellow needles melting at  $177^\circ$ , which are sparingly soluble in ether. On oxidation with dilute nitric acid, benzoic isocymidide yields amidometatoluic acid, which melts below  $100^\circ$ .

*Phthalic metaisocymidide*,  $\text{C}_6\text{H}_4(\text{CO})_2\text{N.C}_{10}\text{H}_{13}$ , is deposited from a hot alcoholic solution in needles, which melt at  $145^\circ$ . The nitro-product forms yellow needles melting at  $167^\circ$ , soluble in alcohol and ether.

*Metaisocyminylocarbamine*,  $\text{C}_{10}\text{H}_{13}\text{NC}$ , prepared by the action of chloroform and alcoholic potash on cymidine, is a colourless liquid having a powerful odour. It is freely miscible with alcohol, ether, benzene, and light petroleum. It cannot be distilled without decomposition. *Metaisocyminylocarbamide*,  $\text{C}_{10}\text{H}_{13}.\text{NH}.\text{CONH}_2$ , is obtained by boiling an excess of potassium isocyanate with a feebly acid solution of cymidine sulphate. It forms lustrous needles melting at  $176^\circ$ , soluble in alcohol. By the action of carbonyl chloride on cymidine dissolved in absolute ether, dimetaisocimynylcarbamide,  $(\text{C}_{10}\text{H}_{13}\text{NH})_2\text{CO}$ , is produced in colourless needles, freely soluble in alcohol, less soluble in ether.

*Metaisocyminylurethane*,  $\text{C}_{10}\text{H}_{13}.\text{NH}.\text{COOEt}$ , is a colourless crystalline compound melting at  $229^\circ$ , soluble in alcohol and ether. *Dicyminylthiocarbamide*,  $(\text{C}_{10}\text{H}_{13}.\text{NH})_2\text{CS}$ , prepared by the action of carbon bisulphide on cymidine, crystallises in needles melting at  $160^\circ$ , soluble in alcohol and ether.

Neither *metaisocyminylethylthiocarbamide*,  $\text{C}_{10}\text{H}_{13}.\text{CSNH}.\text{NH}.\text{Et}$ , nor *metaisocyminylethylguanidine*,  $\text{C}_{10}\text{H}_{13}.\text{C}(\text{NH})\text{NH}.\text{NH}.\text{Et}$ , could be obtained in a crystalline condition.

Nitrophthalylcymidide is decomposed by strong hydrochloric acid at  $180^\circ$ , yielding *nitroisocymidine*,  $\text{NO}_2.\text{C}_{10}\text{H}_{12}.\text{NH}_2$ , an oily liquid miscible with alcohol and ether.

*Metaisocymidinesulphonic acid*,  $\text{C}_{10}\text{H}_{12}(\text{NH}_2).\text{SO}_3\text{H}$ , forms thin yellow-coloured needles, very soluble in water.

The *barium salt*,  $(\text{NH}_2.\text{C}_{10}\text{H}_{12}.\text{SO}_3)_2\text{Ba}$ , also crystallises in needles, which are very soluble in water. W. C. W.

**Action of Dichloroacetic Acid on Aromatic Amines (II).** By P. J. MEYER (*Ber.*, **16**, 2261—2269).—The author previously showed (*Ber.*, **16**, 926) that the reaction of dichloroacetic acid with orthotoluidine is different from that between dichloroacetic acid and paratoluidine, the latter yielding a substituted imesatin. To prepare *paratolylparamethylimesatin* (*paramethylisatin-paratolylimide*),  $\text{C}_8\text{H}_4\text{MeNO.NC}_7\text{H}_7$ , dichloroacetic acid (1 mol.) is heated with paratoluidine (4 mols.) at  $100^\circ$  until a dark-red crystalline mass is formed, which is then treated with hot water to remove the toluidine hydrochloride; or an aqueous or alcoholic solution of dichloroacetic acid may be digested with paratoluidine, or finally dichloroacetamide (1 mol.) heated with paratoluidine (3 mols.). It crystallises in splendid lustrous gold-coloured needles and scales. The reaction may be compared with the formation

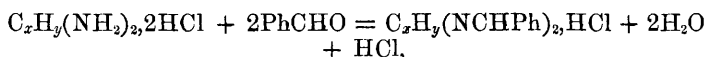
of quinoline from aniline and glycerol (*Ber.*, **13**, 2086):  $2\text{C}_6\text{H}_7\text{NH}_2 + \text{C}_2\text{H}_5\text{Cl}_2\text{O}_2 = \text{C}_{16}\text{H}_{14}\text{N}_2\text{O} + 2\text{HCl} + \text{H}_2\text{O} + \text{H}_2$ . Paramethylisatin-paratolylimide melts at  $259^\circ$ , is insoluble in water, dissolves sparingly in cold, more readily in hot alcohol, and in ether. With concentrated soda solution, it yields a salt crystallising in red prisms, and which is decomposed by water. Cold concentrated hydrochloric acid converts it into paramethylisatin and toluidine; hot dilute acid or long-continued heating with soda solution decomposes it in the same way; it can be reproduced by heating these products with absolute alcohol. When paramethylisatin-paratolylimide is heated for 2 to 3 hours at  $100^\circ$  with alcoholic ammonia, *paramethylimesatin* (*paramethylisatinimide*),  $\text{C}_8\text{H}_7\text{NO.NH}$ , is formed, and can be freed from toluidine and colouring-matter by repeated boiling with alcohol. In its properties, it differs from Laurent's imesatin (*J. pr. Chem.* **25**, 457); it has a pale yellow colour, is insoluble in cold water and cold alcohol, and very sparingly in boiling alcohol, from which it crystallises in extremely slender silky needles; it is not converted into paramethylisatin by acids or bases, and bears a strong resemblance to Sommaruga's diimidoisatin (*Annalen*, **190**, 371; **194**, 85; *Ber.*, **12**, 979). *Paramethylisatin*,  $\text{C}_8\text{H}_4\text{MeNO}_2$ , obtained as above, is isomeric with the substance obtained by Baeyer and Economides (*Ber.*, **15**, 2093) from isatin silver and methyl iodide; it is odourless, separates from alcohol or hydrochloric acid in deep red transparent crystals resembling chromic anhydride, and from water in lustrous red scales, melting at  $187^\circ$ ; it is sparingly soluble in cold, more readily in hot water, readily in hot hydrochloric acid and in alcohol; with alkalis, it forms a deep violet-coloured solution, yielding methylisatates when heated or on long standing. It yields the indophenin-, and with hydroxylamine the ketone-reaction, and forms condensation and substitution-derivatives similar to those of isatin. *Phenylparamethylimesatin* (*paramethylisatinphenylimide*),  $\text{C}_8\text{H}_4\text{MeNO:NPh}$ , is obtained on adding the equivalent quantity of aniline to a concentrated solution of paramethylisatin in absolute alcohol. It crystallises in thick, yellowish-red, transparent plates or prisms, melts at  $239\text{--}240^\circ$ , is sparingly soluble in water or cold alcohol, more readily in hot alcohol, and in its properties resembles paratolylimide. *Metabromoparatolylparamethylimesatin* (*paramethylisatinmetabromoparatolylimide*),  $\text{C}_8\text{H}_4\text{MeNO:NC}_7\text{H}_6\text{Br}$ , is prepared in the same way as the last compound; it crystallises from alcohol in transparent brick-red needles and prisms, melting at  $210^\circ$ . *Orthotolylparamethylimesatin* (*paramethylisatinorthotolylimide*),  $\text{C}_8\text{H}_4\text{MeNO.NC}_7\text{H}_7$ , isomeric with the above paratolylimide, crystallises in red transparent prisms, melting at  $191^\circ$ . *Paramethylnitroso-oxindole*,  $\text{C}_9\text{H}_8(\text{NO})\text{NO}$ , is prepared by the action of hydroxylamine hydrochloride on paramethylisatin (*Ber.*, **16**, 518). It forms long transparent yellow prisms, is sparingly soluble in water, more readily in alcohol, dissolves in potash without decomposition, and melts at  $225\text{--}226^\circ$ . On adding coal-tar benzene to a solution of paramethylisatin in concentrated sulphuric acid, a deep blue coloration is produced, and on agitating with water *paramethylindophenin* separates. The numbers obtained on analysis agree only approximately with the formula  $\text{C}_{13}\text{H}_9\text{NOS}$ . It forms an indigo-blue

powder, sparingly soluble in water, alcohol, and acetic acid, more readily in concentrated sulphuric acid and hot phenol, from which it is reprecipitated by water or alcohol. When treated with zinc and glacial acetic acid, it yields a bright green substance, which becomes blue again on exposure to the air.

A. K. M.

### Difference in Chemical Behaviour of Aromatic Diamines.

By E. LELLMANN (*Annalen*, **221**, 1—34).—The isomeric aromatic diamines, in some cases, present characteristic differences in chemical behaviour. Thus for example, Ladenburg has observed that the hydrochlorides of the orthodiamines react with benzaldehyde according to the equation—



whereas the meta- and para-derivatives are unaltered. Similarly, Hobrecker and Hübner have shown that ortho-diamines are differentiated from the meta- and para-compounds in yielding the so-called

anhydro-bases,  $\text{C}_x\text{H}_y \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C}_y\text{H}_w$ . Again the reaction of nitrous

acid on the ortho- resembles that on the para-, but differs from that which it exerts on the meta-compounds.

The author has studied the reaction of potassium thiocyanate and cyanate, and of the thiocarbimides, on the aromatic diamines, with a view of tracing analogous differences in chemical behaviour.

At the outset some remarks are made on the method of preparation of ortho- and para-phenylene diamines. It is found that to obtain the former it is best to nitrate benzanilide and not acetanilide as recommended in the text-books; on the other hand, acetanilide is more suitable for the preparation of the latter.

*Action of Thiocyanates on the Diamines.*—The diamine thiocyanates are easily obtained from the hydrochlorides of the diamines and the thiocyanates; but the compounds produced differ in their mode of decomposition, the meta- and para-thiocyanate yielding the corresponding phenylenedithiocarbamides,  $\text{C}_6\text{H}_4(\text{NHCSNH}_2)_2$ , whilst the ortho-compounds give the corresponding thiocarbamide,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{CS}$ , together with thiocarbamide,  $\text{CS}(\text{NH}_2)_2$ .

*Orthophenylenethiocarbamide*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{CS}$ , obtained by the evaporation of an aqueous solution of 1 mol. orthophenylenediamine hydrochloride and 2 mols. potassium thiocyanate, crystallises in large leaflets, which melt at about  $290^\circ$  with considerable carbonisation.

*Metaparatolyleneithiocarbamide*,  $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{CS}$ , from metaparatolylene-diamine and potassium thiocyanate, crystallises in silvery leaflets melting at  $284^\circ$ , and soluble in soda and ammonia, but reprecipitated on acidifying the solution.

*Metaphenylenedithiocarbamide*,  $\text{C}_6\text{H}_4(\text{NHCSNH}_2)_2$ , crystallises in microscopic leaflets melting at  $215^\circ$ ; the corresponding para-compound



in colourless needles melting at  $218^{\circ}$ , soluble in alkalis, sparingly soluble in alcohol.

The action of potassium cyanate on the diamines is the same for all three isomerides; a phenylenedicarbamide is formed.

*Orthophenylenedithiocarbamide*,  $C_6H_4(NH.CSNH_2)_2$ , crystallises in hard needles melting at  $290^{\circ}$ , easily soluble in alcohol, sparingly in water, chloroform, or ether. The *para*-compound crystallises in silvery leaflets and decomposes completely at a high temperature without melting; the *meta*-compound crystallises in small colourless needles melting at  $280^{\circ}$ , soluble in concentrated hydrochloric acid, but reprecipitated on the addition of alkalis.

By the action of thiocarbamides on the diamines complex thiocarbamides of the generic formula  $C_xH_y(NH.CSNH.C_vH_w)_2$ , are produced, which in the case of the *ortho*- and *para*-compounds are decomposed, when melted, according to the equation  $C_xH_y(NH.CSNH.C_vH_w)_2 = C_xH_y<\begin{smallmatrix} NH \\ NH \end{smallmatrix}>CS + CS(NH.C_vH_w)_2$ , while the *meta*-compound is unchanged.

*Diphenylmetaparatolylenedithiocarbamide*,  $C_6H_3Me(NH.CSNHPh)_2$ , from tolylenediamine and phenylthiocarbamide, is a crystalline substance which when heated to  $140$ — $150^{\circ}$ , is decomposed into diphenylthiocarbamide subliming in the upper part of the vessel, and metaparatolylenethiocarbamide.

*Diethylmetaparatolylenedithiocarbamide*,  $C_6H_3Me(NH.CSNHEt)_2$ , from ethylthiocarbamide and tolylenediamine forms microscopic crystals which melt between  $149^{\circ}$  and  $153^{\circ}$ , and on more protracted heating are decomposed into metaparatolylene- and ethylthiocarbamides. The former is a crystalline substance melting at  $284^{\circ}$ , sparingly soluble in water, easily soluble in alcohol and hot soda. *Diallylmetaparatolylenedithiocarbamide*,  $C_6H_3Me(NH.CSNH.C_3H_5)_2$ , from tolylenediamine and allylthiocarbamide, crystallises in delicate silky needles, melting at  $150^{\circ}$ , sparingly soluble in water, soluble in alcohol and chloroform.

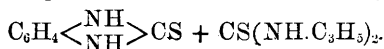
The corresponding *diallylmetaphenylenedithiocarbamide*,



forms an amorphous white powder, which melts at  $105^{\circ}$ , and is not decomposed when heated. *Diphenylparaphenylenedithiocarbamide*,  $C_6H_4(NH.CSNHPh)_2$ , is a crystalline substance, soluble in hot soda solution. When heated to  $260^{\circ}$  it is decomposed partly into paraphenylenethiocarbamide,  $C_6H_2<\begin{smallmatrix} NH \\ NH \end{smallmatrix}>CS$ , which crystallises in small leaflets, melting at  $270^{\circ}$ . *Diallylparaphenylenedithiocarbamide*,



is a crystalline substance, insoluble in water, sparingly soluble in alcohol. It melts at  $200^{\circ}$ , with evolution of a gas and emission of a smell resembling diallylthiocarbamide: its decomposition may probably be expressed by the equation,  $C_6H_4(NH.CSNH.C_3H_5)_2 =$



The author also made some experiments on the reduction of the orthonitranilides and toluides of phenylsulphonic acid. When phenylsulphonyl chloride is added to orthonitraniline dissolved in benzene, crystals of orthonitraniline hydrochloride separate out. On filtering these and evaporating the filtrate, *phenylsulphorthonitranilide*,



is obtained. This substance is crystalline, moderately soluble in petroleum, easily soluble in alcohol; it is reduced by tin and hydrochloric acid to the corresponding *amidoanilide*,  $\text{PhSO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ . This compound crystallises in long colourless needles melting at  $168^\circ$ , sparingly soluble in water, readily soluble in alcohol and chloroform; its hydrochloride forms large thick crystals. *Phenylsulphometanitroparatoluide*,  $\text{PhSO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2$ , obtained together with the corresponding dinitro-derivative by the action of fuming nitric acid on phenylsulphoparatoluide, crystallises in cubes, which melt at  $99^\circ$ . On reduction with tin and hydrochloric acid, it is converted into the corresponding amido-derivative, which crystallises in long, colourless needles, melting at  $146\cdot5^\circ$ , sparingly soluble in water, soluble in alcohol.

In a summary, the author remarks that the above observations do not form sufficient material for general conclusions with regard to the reactions of the diamines. To complete the study of these compounds, it is necessary to compare the decomposition of the isomeric phenylenediamines with the diamines of the paraffin series. As a step in this direction, Hofmann has observed that ethylenediaminethiocyanate when melted yields ethylenethiocarbamide, a decomposition perfectly analogous to the decomposition of the corresponding orthodiphenylene compound.

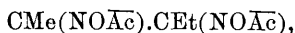
V. H. V.

**Organic Hydroxylamine Derivatives.** By C. SCHRAMM (*Ber.*, 16, 2183—2188).—When a solution of bromacetophenone in aqueous alcohol is heated with an excess of hydroxylamine hydrochloride for 12 hours on a water-bath, the alcohol evaporated, and the product extracted with ether, a yellowish oil is obtained which solidifies on standing. It can be purified by precipitating its solution in soda with dilute sulphuric acid and extracting with ether; it then melts at  $162-163^\circ$ . Its formula is  $\text{CPh}(\text{N}\cdot\text{OH})\cdot\text{CH}_2\cdot\text{NH}\cdot\text{OH}$ . It dissolves readily in alcohol or ether, sparingly in hot water and benzene, and is insoluble in light petroleum and in cold water. On heating it with concentrated acids, hydroxylamine is given off. A *silver derivative*,  $\text{C}_8\text{H}_9\text{AgN}_2\text{O}_2$ , is obtained by precipitating a solution in concentrated ammonia with a concentrated solution of silver nitrate. *Dibenzylhydroxylamine*,  $(\text{CH}_2\text{Ph})_2\text{N}\cdot\text{OH}$ , is obtained on heating a solution of benzyl chloride (3 grams), hydroxylamine hydrochloride (3 grams), and crystallised sodium carbonate (6 grams) in aqueous alcohol for half an hour on a water-bath. On cooling, it separates in long white needles which melt at  $123^\circ$ , and are decomposed by distillation. It is soluble in alcohol, ether, and benzene, less soluble in light petroleum, carbon bisulphide, and glacial acetic acid, sparingly in hot water, and insoluble in ammonia, soda solution, and hydrochloric acid. A *hydrochloride*,

$(C_7H_7)_2N.OH.HCl$ , can be obtained by the action of dry hydrochloric acid gas on its solution in absolute ether.

*Methylpropylglyoxime*,  $CMe(NO.H).C(NO.H)Pr$ , obtained by the action of hydroxylamine hydrochloride on a solution of isonitrosopropylacetone in aqueous alcohol, forms spiral-like groups of needles melting at  $168^\circ$ . *Phenylglyoxime*,  $CPh(N.OH).CH:N.OH$  (m. p.  $152^\circ$ ) is prepared by the action of alkaline hydroxylamine solution on dibromacetophenone, at a gentle heat, acidifying and extracting with ether. It can be purified by precipitating the ethereal solution with light petroleum and washing the precipitate with benzene, or by dissolving it in alkali, acidifying and extracting with ether. The *silver derivative*,  $C_6H_5AgN_2O_2$ , forms a yellowish-white curdy precipitate. On dissolving sodium in absolute alcohol and adding an ethereal solution of methylethylglyoxime, the *sodium derivative* of the latter,  $C_6H_5NaN_2O_2$ , is thrown down as a white curdy precipitate. The *diacetyl-derivative of methylglyoxime*,  $CMe(NOAc).CH(NOAc)$  is formed when a mixture of *methylglyoxime* with a slight excess of acetic anhydride is gently boiled until the mass begins to turn brown. The product is poured into shallow clock-glasses and exposed in a vacuum when needles are obtained melting at  $51^\circ$ . It crystallises from light petroleum in white transparent prisms; when heated, these explode with evolution of hydrocyanic acid.

The *diacetyl-derivative of methylethylglyoxime*,

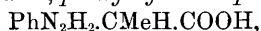


crystallises in flat prisms readily soluble in alcohol and in ether, sparingly in hot water. The *diacetyl-derivative of methylbenzylglyoxime* forms small white crystals melting at  $80^\circ$ . A. K. M.

**Hydrazines of Pyrroacemic Acid.** By E. FISCHER and F. JOURDAN (*Ber.*, **16**, 2241—2245).—Some of the compounds of the hydrazines with ketones have been described by Reisenegger (*Abstr.*, 1883, 798). The reaction is a general one, and holds for the primary and secondary hydrazines of the fatty and aromatic series, and for all simple and most of the more complicated ketones and diketones, the ketonic acids combining with extreme readiness with the hydrazines either in neutral or in acid solutions. Pyrroacemic acid and phenylhydrazine combine with great violence, so that it is advisable to dilute each substance with five volumes of ether, to cool well and to mix gradually.

The *phenylhydrazinepyrroacemic acid*,  $C_9H_{10}N_2O_2$ , separates as a yellowish crystalline powder which after being washed with ether and crystallised from boiling alcohol, forms hard lustrous needles, melting at  $169^\circ$  with evolution of gas; it is readily soluble in hot alcohol, very sparingly in ether, chloroform, carbon bisulphide, and light petroleum, readily in alkalis and alkaline carbonates. The sodium salt is sparingly soluble in an excess of concentrated soda solution, with which it can be boiled without decomposition. The formation of phenylhydrazinepyrroacemic acid takes place also in aqueous, acetic acid, and dilute hydrochloric acid solutions, and with such readiness that the reaction can be employed for the detection of pyrroacemic

acid (also of phenylglyoxylic acid and levulic acid) in very dilute solutions. Heated above its melting point, it yields carbonic anhydride and ethylidenephénylhydrazine:— $\text{PhN}_2\text{H}:\text{CMe}.\text{COOH} = \text{CO}_2 + \text{PhN}_2\text{H}:\text{CHMe}$ . It can be boiled with dilute hydrochloric and sulphuric acids without decomposition, and on boiling with alcoholic sulphuric acid, the *ethyl derivative*,  $\text{PhN}_2\text{H}:\text{CMe}.\text{COOEt}$ , is obtained melting at  $114-115^\circ$ , and soluble in alcohol, ether, and chloroform. By the action of sodium-amalgam on a cold dilute solution of phenylhydrazinepyrroacemic acid, *phenylhydrazinepropiotic acid*,



is produced, crystallising from boiling alcohol in white slender needles melting at  $152-153^\circ$  with decomposition. It is very sparingly soluble in cold alcohol, ether, and water, much more readily in hot alcohol, also readily soluble in alkalis and in concentrated hydrochloric acid. Mercuric oxide and copper salts are readily reduced by it in alkaline solution, ammoniacal copper solution reconverting it into phenylhydrazinepyrroacemic acid.

In order to decide which of the formulæ  $\text{PhNH.N}:\text{CMe}.\text{COOH}$  or  $\text{PhN}-\text{CMe}.\text{COOH}$  is correct, the action of pyrroacemic acid on



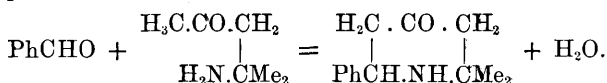
methylphenylhydrazine was studied. This yields an acid of the formula  $\text{PhNMe.N}:\text{CMe}.\text{COOH}$ , the behaviour of which to mineral acids is, however, quite different from that of the acid obtained from phenylhydrazine.

*Methylphenylhydrazinepyrroacemic acid* softens at  $70^\circ$ , and melts at  $78^\circ$ ; it crystallises in yellowish needles readily soluble in alcohol and in ether, sparingly in light petroleum and in water; it is decomposed by long-continued boiling with water, but is stable in alkaline solutions. On warming it with a 10 per cent. solution of hydrochloric acid it becomes red, and then dissolves, the colour disappearing as the temperature is raised, whilst colourless slender needles separate, increasing in quantity on cooling and as the liquid is diluted with water. This new substance, apparently of the formula  $\text{C}_{10}\text{H}_9\text{NO}_2$ , seems to be formed by the abstraction of ammonia from the methylphenylhydrazinepyrroacemic acid, a considerable quantity of ammonia being found in the acid liquid. It is readily soluble in hot alcohol, from which it crystallises in colourless needles melting at  $206^\circ$ . It can be distilled unchanged, dissolves readily in soda, ammonia, and sodium carbonate, and can be reprecipitated by acids. A. K. M.

**Diacetonamine.** By E. FISCHER (*Ber.*, **16**, 2236—2238).—In preparing diacetonamine from acetone containing aldehyde, Heintz (*Annalen*, **189**, 214) obtained a base  $\text{C}_8\text{H}_{15}\text{NO}$ , (vinyl diacetonamine); this he afterwards obtained by the action of acetaldehyde on diacetonamine oxalate, and he thought it probable that it might be a lower homologue of triacetonamine; this is now confirmed by the author. It is converted into an alkamine by the action of sodium-amalgam, and on heating this with concentrated sulphuric acid, a readily volatile base is obtained, the properties of which show it to be a homologue of triacetonine (*Abstr.*, 1883, 1153).

Other aldehydes, both of the fatty and aromatic series, yield bases with diacetoneamine, and in this way numerous homologues of hydroxypiperidine and piperidine can be obtained. *Benzdiacetoneamine*,  $C_{13}H_{17}NO$ , is prepared by boiling a solution of acid diacetoneamine oxalate (1 part) in alcohol (3 parts) with bitter almond oil (1 part) for about ten hours; the product is filtered hot, and the oxalate formed is washed with hot alcohol. By the action of potash the free base is obtained as an oil, which solidifies on standing; it crystallises from hot light petroleum in splendid colourless plates, melts at  $62-63^{\circ}$ , dissolves very readily in alcohol and in ether, sparingly in water; the *oxalate*  $(C_{13}H_{17}NO)_2C_2H_2O_4$ , forms white scales, very sparingly soluble in alcohol and in water, readily in hydrochloric and oxalic acids. On adding gold chloride to the hydrochloric acid solution, the aurochloride is precipitated as a yellow oil, which solidifies to magnificent gold-coloured needles. By the action of sodium-amalgam on an acidulated solution of benzdiacetoneamine, the latter is partially converted into *benzdiacetonealkamine*,  $C_{13}H_{19}NO$ . The hydrochloride,  $C_{13}H_{19}NO \cdot HCl$ , forms small hard crystals, readily soluble in water, sparingly in alcohol. On decomposing it with an alkali, the base is precipitated as a thick colourless oil. Sulphuric acid acts on this base or the hydrochloride in the same way as on triacetonealkamine, with formation of a new base, which is volatile in steam, has an odour resembling that of piperidine, and yields a sparingly soluble hydrobromide.

From these reactions, it is assumed that benzdiacetoneamine has a constitution similar to that of triacetoneamine, its formation being thus expressed:—



The author intends to try the reaction with other aldehydes, with ethyl acetoacetate, and with pyrrolacetic and other ketonic acids.

A. K. M.

**Action of Phosphorus Trisulphide on Phenols.** By A. GEUTHER (*Annalen*, **221**, 55–59).—Kekulé and Szuch (*Jahresber.*, 1868, 628) have isolated from the products of the reaction of phosphorus pentasulphide on phenol, besides phenyl mercaptan and sulphide, a small quantity of benzene. As the formation of this hydrocarbon can only arise from the reduction of the phenol, it is probable that the samples of pentasulphide contained some trisulphide as an impurity. In order to confirm this suggestion, the author has studied the action of phosphorus trisulphide on phenol. On submitting the crude product of the reaction to fractional distillation, it was separated into two portions, the one boiling below  $100^{\circ}$ , the other above  $280^{\circ}$ . The former was principally benzene, together with traces of phenyl mercaptan and sulphide, the latter triphenylphosphate. The reactions of phosphorus trisulphide and pentasulphide on phenol may probably be expressed by the following equations:—(1)  $8\text{PhOH} + \text{P}_2\text{S}_3 = 2\text{Ph}_3\text{PO}_4 + 3\text{H}_2\text{S} + 2\text{C}_6\text{H}_6$ , and (2)  $8\text{PhOH} + \text{P}_2\text{S}_5 = 2\text{Ph}_3\text{PO}_4 + 3\text{H}_2\text{S} + 2\text{PhSH}$ .

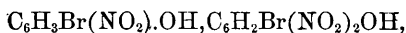
As an analogous case, it is shown that cresol is similarly reduced to toluene by phosphorus trisulphide; the other products of the reaction, which were not minutely examined by the author, are probably tolyl mercaptan and tolylphosphate.

V. H. V.

**A Fourth Monobromophenol.** By A. FITTICA (*J. pr. Chem.* [2], 28, 176—188).—10 grams of phenol are dissolved in 10 grams absolute alcohol, 3 grams of amorphous phosphorus added, and 17 grams of bromine allowed to flow in through a capillary tube; the vessel is surrounded with cold water; the temperature of the mixture must not rise above 20°. The product is shaken with water, with dilute sodium carbonate, again with water, dried and distilled. The fraction 235—240° repeatedly redistilled, finally yields the new monobromophenol as a liquid boiling at 236—238°, and not solidifying at 10—12°. The pure substance cannot be distilled without decomposition. No further description of its properties is given. The boiling and melting points of ortho-, meta-, and para-bromophenol are—

	Ortho.	Meta.	Para.
Melting point . . . .	(Liquid)	32—33°	64°
Boiling point. . . . .	194—195°	236—236.5	238

By nitration in glacial acetic acid solution, a crystalline compound melting at 60—65°, and of the formula



is obtained. This on further nitration yields a bromodinitrophenol,  $\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)_2.\text{OH}$ , crystallising in yellow prisms, and melting at 108—110°. The same product is obtained on boiling with baryta-water, together with a substance melting at 68—70°, and crystallising in stellate groups of yellow needles, to which the author assigns the formula  $2\text{C}_6\text{H}_3\text{Br}(\text{NO}_2).\text{OH}, \text{C}_6\text{H}_2\text{Br}(\text{NO}_2)_2.\text{OH}$ .

A. J. G.

**Action of Phenol on Ketonic Acids.** By C. BÜTTINGER (*Ber.*, 16, 2071—2075).—By the action of phenol on pyroracemic acid in presence of sulphuric acid, a condensation-product of the composition  $\text{C}_{15}\text{H}_{14}\text{O}_4, \text{H}_2\text{O}$  is obtained. This substance, which the author proposes to name *diphenylpropionic acid*, forms a horny mass (m. p. 268°), soluble in acetone, insoluble in water, benzene, and chloroform. It is a monobasic acid, and a solution of its ammonium salt gives precipitates with salts of barium, calcium, lead, and silver.

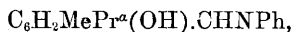
*Dibromophenopropionic acid* is a pale golden amorphous and electric powder, insoluble in water and alcohol; on heating this with concentrated hydrochloric acid at 230° in a sealed tube, it gives off bromine and carbonic anhydride, and is converted into a black substance.

*Acetyldiphenopropionic acid* is an amorphous yellowish substance, soluble in acetone, insoluble in chloroform; its barium salt forms an insoluble amorphous precipitate.

*Acetyldibromophenopropionic acid* is coloured at first violet, and then dissolved by ammonia; it forms sparingly soluble barium salt.

V. H. V.

**Derivatives of Thymol.** By H. KOBEK (*Ber.*, **16**, 2096—2105).—*Parathymotic aldehyde*,  $C_6H_2MePr^a(OH).CHO$  (Me : OH : Pr : CHO = 1 : 3 : 4 : 6) obtained by heating thymol with chloroform and soda, crystallises in long white glistening needles melting at  $133^\circ$ , sparingly soluble in water, soluble in alcohol and ether. It dissolves in ammonia and sodium carbonate to form a golden-coloured solution. The author was unable to obtain a crystalline compound of the substance with sodium hydrogen sulphite; but its other general properties characterise it as an aldehyde. Its *anilide* derivative,

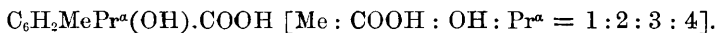


prepared by heating parathymotic aldehyde and aniline in molecular proportions, crystallises in golden needles melting at  $142^\circ$ , insoluble in water, soluble in alcohol and ether; it is decomposed by boiling with water or dilute acids into the aldehyde and aniline.

*Parathymotic alcohol*,  $C_6H_2MePr^a(OH).CH_2.OH$ , obtained by the reduction of the aldehyde with sodium-amalgam and water, forms a greyish amorphous powder, which melts gradually at  $120-130^\circ$ ; it is insoluble in water, soluble in alcohol and ether.

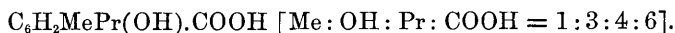
*Methylparathymotic aldehyde*,  $C_6H_2MePr^a(OMe).CHO$ , prepared from parathymotic aldehyde, methyl iodide, and alcohol, is a golden oil boiling at  $270^\circ$ , insoluble in water, soluble in alcohol and ether; it dissolves with difficulty in a solution of sodium hydrogen sulphite. Its *anilide* crystallises in clear transparent tablets (m. p.  $80^\circ$ ), insoluble in water, readily soluble in other menstrua. On oxidation with potassium permanganate, it is converted into the corresponding *carboxylic acid*,  $C_6H_2MePr(OMe).COOH$ , which crystallises in long white silky needles melting at  $137^\circ$ ; a solution of this acid gives no coloration with ferric chloride, and precipitates more or less sparingly soluble, with salts of calcium, silver, copper, zinc, and lead.

In order to determine the constitution of the compounds, and to compare the parathymotic acid corresponding with the above-mentioned aldehyde with the thymotic acid described by Kolbe and Lautemann (*Annalen*, **115**, 205), the author prepared both acids, and studied their reactions. The former can be best obtained by heating thymol with carbon tetrachloride and soda; it crystallises in leaflets melting at  $157^\circ$ ; the latter by the joint action of sodium and carbonic anhydride on thymol melts at  $123^\circ$  and gives a deep blue coloration with ferric chloride. This reaction, characteristic of those aromatic acids in which the hydroxyl is in the ortho-position to the carboxyl group, taken in connection with the method of preparation, shows that the thymotic acid of Kolbe and Lautemann is the ortho-acid, possessing the constitution



On the other hand, the method of preparation of the author's acid,

together with the absence of any reaction with ferric chloride, point probably to its constitution as expressible by the formula



*Thymodialdehyde*,  $\text{C}_6\text{H}_2\text{MePr}(\text{OH})(\text{CHO})_2$ , obtained in the course of the preparation of parathymotic aldehyde, forms golden compact needles melting at  $80^\circ$ ; it gives a cherry-red coloration with ferric chloride; on boiling with sodium acetate and acetic anhydride it is converted into *thymoparacrylic acid*,  $\text{C}_6\text{H}_2\text{MePr}(\text{OH}).\text{CH} : \text{CH}.\text{COOH}$ , which forms microscopic crystals melting at  $280^\circ$ . The *methyl* derivative of the latter crystallises in golden needles melting at  $141^\circ$ , sparingly soluble in water, soluble in alcohol and ether. Both acids give sparingly soluble calcium, barium, and copper salts; their silver salts, however, differ, that of the former crystallises from water, that of the latter dissolves in hot water, forming a resinous mass.

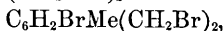
V. H. V.

**A New Glycerol.** By A. COLSON (*Compt. rend.*, **97**, 177—179).—The aromatic tribromhydrin,  $\text{C}_6\text{H}_3(\text{CH}_2\text{Br})_3$ , previously described (Abstr., 1883, 734), can be obtained in crystals by prolonged refrigeration, and the crystals, after recrystallisation from alcohol, melt at  $94.5^\circ$ . The tribromhydrin is decomposed by water, yielding *mesitylene glycerol*,  $\text{C}_6\text{H}_3(\text{CH}_2.\text{OH})_3$ . To obtain this compound, the crude product of the action of bromine on mesitylene is boiled for several hours with 25—30 parts of water and an excess of lead carbonate, the liquid filtered, and concentrated by evaporation in a vacuum. The crude product is mixed with a small quantity of silver oxide, then treated with hydrogen sulphide in order to remove lead, and the solution filtered and concentrated. The viscous liquid thus obtained is purified by successive treatment with ether, alcohol, and chloroform, and is finally concentrated in a vacuum. Mesitylene glycerol is a viscous liquid with a bitter taste; it is insoluble in ether and in chloroform, but is very soluble in alcohol and in water. When treated with hydrobromic acid, it yields the original tribromhydrin. Hydrochloric acid forms a colourless oily liquid, which is in all probability the trichlorhydrin: the same compound is obtained by the action of chlorine on the vapour of mesitylene; it boils at  $170$ — $180^\circ$  in a vacuum, and at  $277$ — $284^\circ$  with partial decomposition, under atmospheric pressure. It is decomposed by water with formation of the glycerol. Acetic acid also combines with mesitylene glycerol, forming a compound which is only slightly soluble in water.

If the product of the saponification of the crude tribromhydrin is treated with ordinary ether after evaporation of the water, the ether dissolves a substance which separates out in crystals on evaporation. When purified by repeated crystallisation from water, this substance forms nacreous plates which melt at  $126^\circ$ . They are tasteless and inodorous, soluble in 55 parts of boiling water, but only slightly soluble in cold water, still less soluble in ether, but very soluble in alcohol. They have the composition,  $\text{C}_9\text{H}_9(\text{OH})_2\text{Br}$ ; when boiled with water and potassium carbonate, this compound is not decomposed; and when treated with hydrobromic acid it yields a tribromide which, after recrystallisation from alcohol, melts at  $81$ — $82^\circ$ . The compound



is therefore not a derivative of mesitylene glycerol, but is a monobromo-glycol,  $C_6H_2BrMe(CH_2.OH)_2$  and its dibromohydrin,



(m. p.  $81-82^\circ$ ), is isomeric with mesitylene glycerol tribromhydrin.

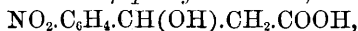
C. H. B.

**Quinone Derivatives.** By R. NIETSKI (*Ber.*, **16**, 2092—2096).—The author has shown that by passing nitrous acid into an ethereal solution of quinol, a dinitrohydroxyquinone,  $C_6(OH)_2(NO_2)_2O_2$ , or nitranilic acid, is formed; the same substance may also be obtained either by the action of fuming nitric acid on dinitroquinol, or by the nitration of diacetylquinol; all these methods of preparation, however, are very unsatisfactory. In the present communication a detailed account is given of an improved process, which consists in acting on diacetylquinol with nitrosulphuric acid in the cold, and precipitating the characteristic sparingly soluble potassium nitranilate from an ice-cold solution of the crude product. The corresponding acid, which is very unstable, may be obtained from this derivative. The potassium-derivative is converted by a strongly acid solution of stannous chloride into nitramidotetrahydroxybenzene,  $C_6(OH)_4(NH_2).NO_2$ , which crystallises in needles, having a violet iridescence, insoluble in alcohol, ether, and benzene. Potassium nitranilate is further converted by stannous chloride, with an excess of tin, into a substance crystallising in delicate iridescent green leaflets, resembling quinhylol in appearance. This compound is probably a diimido-derivative of dihydroxy-

quinone,  $C_6(OH)_2O_2 \begin{array}{c} \text{NH} \\ \diagdown \quad | \\ \text{NH} \end{array}$ , and analogous to diimidonaphthol: a

view which receives some support from the similarity of phenomena observable in the preparation of these two substances. V. H. V.

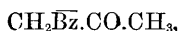
**Action of Orthonitrobenzaldehyde on Acetaldehyde.** By A. BAEYER and V. DREWSSEN (*Ber.*, **16**, 2205—2208).—In a previous communication (*Abstr.*, 1883, 341) the authors mentioned the formation of a condensation-product by the action of alkalis on a solution of orthonitrobenzaldehyde in acetaldehyde. It is prepared by gradually adding a 2 per cent. solution of sodium hydroxide to a solution of orthonitrobenzaldehyde in freshly prepared aldehyde kept cool with ice, until an alkaline reaction remains for at least five minutes. The acetaldehyde is expelled by a current of air, the crystalline product dried on a porous tile and crystallised from ether. It forms moderately large colourless monoclinic prisms, readily soluble in alcohol and chloroform; it softens at  $120^\circ$  and melts at  $125^\circ$  with evolution of aldehyde vapour. Its formula,  $C_9H_9NO_4.C_2H_4O$ , corresponds with that of a compound of orthonitrophenyllactic aldehyde with aldehyde. On passing a current of air through its solution at  $40-50^\circ$ , as long as the odour of aldehyde is perceptible, a non-crystallisable product is obtained (probably *orthonitrophenyllactic aldehyde*), combining with acid sulphites and reddening rosaniline sulphite. Like the condensation-product, it yields indigo with aqueous alkalis. *Orthonitro-β-phenyllactic acid*,



(m. p.  $126^{\circ}$ ) is obtained on warming a solution of the condensation-product in dilute alcohol with an excess of freshly precipitated silver oxide, until the addition of alkali no longer produces indigo; the product is boiled with hydrochloric acid, filtered, and extracted with ether, and the acid purified by means of the barium salt. It crystallises in short well-formed prisms, readily soluble in water, alcohol, and ether, and is identical with the acid obtained by Einhorn from the addition-product of orthonitrocinnamic acid with hydrobromic acid (see p. 66). *Orthonitrocinnamic aldehyde*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CHO}$ , is obtained on boiling the condensation-product with acetic anhydride until indigo ceases to be formed by the addition of soda solution. It forms colourless needles melting at  $127^{\circ}$ , readily soluble in boiling water, very sparingly in cold water, readily in chloroform, less so in alcohol and ether. It forms a crystalline compound with hydrogen-sodium sulphite, reacts with rosaniline sulphite, reduces ammoniacal silver solution with formation of orthonitrocinnamic acid, and on reduction readily yields quinoline. From the above, it is seen that the condensation of orthonitrobenzaldehyde with aldehyde takes place in the same way as with acetone, the resulting orthonitro- $\beta$ -phenyllactic aldehyde,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{COH}$ , forming, however, an unstable compound with acetaldehyde.

A. K. M.

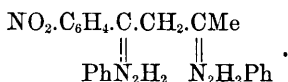
**Benzoylacetone.** By E. FISCHER and H. KUZEL (*Ber.*, **16**, 2239—2241).—On boiling ethyl benzoylacetacetate with 4 parts of 25 per cent. sulphuric acid, carbonic anhydride, alcohol, acetic acid, and acetophenone are produced as stated by Bonn  (*Annalen*, **187**, 1). The authors find that a small quantity of benzoic acid and about 4 per cent. of *benzoylacetone* are also produced, the formation of the latter corresponding with the production of nitrocinnamylacetone from ethyl nitrocinnamylacetacetate (*Abstr.*, 1883, 587). To isolate the benzoylacetone, the oil is dissolved in ether, agitated with dilute soda solution, which dissolves the benzoic acid and the benzoylacetone; the solution is then acidified, extracted with ether, and the residue from the evaporation of the latter dissolved in cold dilute soda solution, from which the benzoylacetone is precipitated by carbonic anhydride as a colourless oil, which crystallises on cooling. It may be obtained in larger quantity by boiling ethyl benzoylacetacetate for some hours with 7—8 parts water. Benzoylacetone,



melts at  $58^{\circ}$ , distils unchanged, is volatile in steam, and has an agreeable penetrating odour. It dissolves sparingly in cold water, more readily in hot water, very readily in alcohol and in ether. The alkalis dissolve it readily, sodic carbonate less so, whilst it is insoluble in the acid carbonates. The sodium salt of benzoylacetone is precipitated in the form of yellowish scales on adding concentrated alkali to its solution in dilute soda; the silver salt,  $\text{C}_{10}\text{H}_9\text{O}_2\text{Ag}$ , obtained on adding an excess of silver nitrate to an ammoniacal solution of benzoylacetone, forms a white crystalline precipitate, almost insoluble in water. Benzoylacetone gives an intense red coloration with ferric chloride. It is decomposed by boiling alkali with formation of acetophenone.

When warmed with phenylhydrazine, the two combine forming a slightly coloured oily product insoluble in alkali.

*Orthonitrobenzoylacetone* is obtained in the same way from ethyl orthonitrobenzoylacetate, and likewise combines with phenylhydrazine, forming a compound of the formula—



The behaviour of benzoylacetone with alkalis shows that the hydrogen of the methylene-group can be substituted by metals, which is not the case with the hydrazine-derivatives in which the oxygen of the CO-groups is replaced by nitrogen. A. K. M.

**Anthroxanaldehyde and Anthroxanic Acid.** By A. SCHILLINGER and S. WLEÜGEL (*Ber.*, 16, 2222—2226).—When a solution of orthonitrophenylhydroxyacrylic acid in an equal weight of glacial acetic acid is heated on a water-bath as long as carbonic anhydride is evolved, and then diluted with water, neutralised with chalk, and steam-distilled, a distillate is obtained from which ether extracts *anthroxanaldehyde* mixed with anthranil; the latter is removed by boiling with light petroleum, from which solvent anthroxanaldehyde crystallises in long yellowish needles of a slightly aromatic and penetrating odour; it dissolves readily in boiling water, and volatilises easily in steam. It melts at 72·5°, and can be sublimed without decomposition. Its formula,  $\text{C}_8\text{H}_5\text{NO}_2$ , shows it to be isomeric with isatin. An intense reddish-violet coloration is produced on adding zinc-dust to its solution in very dilute ammonia and warming. When an aqueous solution, containing also anthranil, is boiled with ferrous sulphate, slender red silky needles separate, which, after crystallisation from chloroform, contain no iron; this substance melts above 215° with decomposition; it has basic properties. Anthroxanaldehyde dissolves readily in concentrated hydrogen-sodium sulphite, and produce a red coloration with rosaniline sulphite. When it is warmed with aniline, an oil is obtained which solidifies to large fan-shaped crystals, melting at about 40°. *Anthroxanic acid*,  $\text{C}_8\text{H}_5\text{NO}_3$ , is prepared by adding the calculated quantity of a 4 per cent. permanganate solution to a cold solution of the aldehyde in very dilute soda, filtering and slightly acidifying. The solution is warmed with animal charcoal, filtered, and dilute sulphuric acid added, when *anthroxanic acid* separates in delicate white needles. It is moderately soluble in hot water, almost insoluble in cold water, readily in acetone, more sparingly in glacial acetic acid, and still less readily in benzene and other solvents. It melts at 190—191° with decomposition. On warming its solution in dilute ammonia with ferrous sulphate, filtering and acidulating, isatin is obtained.

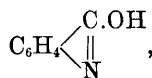
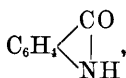
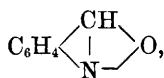
The authors assign to this acid the constitution  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C} \diagdown \\ | \quad \text{O} \\ \text{N} \end{array} \cdot \text{COOH}$ ,  
analogous to isatogenic acid,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \cdot \text{C} \cdot \text{COOH} \\ | \quad | \\ \text{N} \quad \text{O} \end{array}$ , which it resembles

in its behaviour to feeble reducing agents. Unsuccessful attempts were made to decompose it into carbonic anhydride and *anthroxane*,

$\text{C}_6\text{H}_4 \begin{array}{c} \text{CH} \\ | \\ \text{N} \end{array} \text{O}$ , which, if capable of existing, would be isomeric with

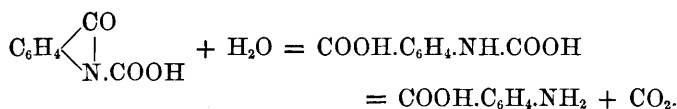
anthranil. Possibly anthroxane becomes converted into the latter in the same way as isatogen into isatin. A. K. M.

**Constitution of Anthranil.** By P. FRIEDLÄNDER and S. WLEÜGEL (*Ber.*, 16, 2227—2229).—From the close relationship of anthranil to anthroxanic acid (see last Abstract) an attempt was made to prepare the latter by heating anthranil with ethyl chlorocarbonate at 120—140°. Of the three possible formulæ for anthranil—



the first alone could yield anthroxanic acid, the second an isomeric anthranilcarboxylic acid, whilst the third could not yield a carboxylic acid.

The product of the reaction was an acid (*anthranilcarboxylic acid*) isomeric with anthroxanic acid, but possessing different properties. It dissolves sparingly in the usual solvents, most readily in acetone and in ether, and crystallises from hot water in slender needles melting at about 230° with evolution of carbonic anhydride, but anthranil is not re-formed. The presence of a carboxyl-group is proved by its solubility in dilute ammonia and in alkaline carbonates, mineral acids reprecipitating it unchanged. It dissolves in a one per cent. soda solution, showing a blue fluorescence which soon disappears, and on then acidifying with acetic acid and extracting with ether, the equivalent quantity of *anthranilic acid* is obtained. This change probably takes place thus:—



Anthranilcarboxylic acid is decomposed by hot concentrated soda solution, with formation of anthranilic acid and of a high-melting acid, probably a derivative of diphenylcarbamide.

On gently heating a mixture of dry anthranil with benzoic chloride, an abundant evolution of hydrochloric acid takes place, whilst *benzoyl-*

*anthranil*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ | \\ \text{N.COPh} \end{array}$ , is formed. The product crystallises on

cooling, and can be purified by recrystallisation from dry benzene with the addition of light petroleum. It forms long white needles readily soluble in the ordinary solvents, insoluble in water and light petroleum; it melts at 122—123°, and distils above 360° nearly unchanged. Like anthranil, it readily takes up the elements of water

with formation of *benzoylanthranilic acid*,  $\text{COOH.C}_6\text{H}_4.\text{NH.COPh}$ ; the change being effected by solution in hot dilute alkalis or by crystallisation from dilute alcohol, when the melting point is raised from  $123^\circ$  to  $180$ — $181^\circ$ . The benzoylanthranilic acid obtained is identical with the acid obtained from anthranilic acid and benzoic chloride (*Annalen*, **205**, 130). It yields sparingly soluble *barium* and *calcium salts*, and a nearly insoluble stable *silver salt*,  $\text{C}_{14}\text{H}_{10}\text{NO}_3\text{Ag}$ .

These results prove that anthranil is represented by the second of the above formulæ, and that it is the lactam of anthranilic acid.

A. K. M.

**Action of Hydroxylamine on Diketones.** By H. GOLDSCHMIDT (*Ber.*, **16**, 2176—2180).—The author and V. Meyer have isolated and described a diphenylglyoxime (m. p.  $237^\circ$ ),  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$ , obtained by the action of hydroxylamine on benzil. Under other conditions, the author has obtained an isomeride which in contradistinction to the first named substance may be called  $\beta$ -diphenylglyoxime; it differs from its isomeride in its melting point ( $206^\circ$ ), its appearance, and its greater solubility in water and alcohol. The  $\alpha$ -glyoxime may be converted into the  $\beta$ -isomeride by heating to  $180^\circ$ .

On heating phenanthraquinone with alcohol and hydroxylamine hydrochloride, a monisonitroso-derivative of phenanthraquinone,  $\text{C}_{14}\text{H}_9\text{NO}_2$ , is formed.

This substance crystallises in small golden needles melting at  $158^\circ$ , soluble in alcohol; it dissolves in soda to form a green, and in sulphuric acid to form a red solution. It is converted by hydroxylamine hydrochloride into a dioxime derivative of phenanthraquinone, of

possible constitution,  $\begin{array}{c} \text{C}_6\text{H}_4.\text{C}:\text{N} \\ | \quad | \\ \text{C}_6\text{H}_4.\text{C}:\text{N} \end{array} \rangle \text{O}$ , which crystallises in golden

needles melting at  $181^\circ$ , insoluble in soda. When anthraquinone is heated with alcohol and hydroxylamine hydrochloride, in a flask fitted with an inverted condenser, no reaction takes place.

In order to obtain the monisonitroso-derivative of anthraquinone, it is necessary to heat the reacting substances in a sealed tube at  $180^\circ$ , when the compound separates out as a pale red powder, soluble in alcohol, to form a red solution. It sublimes at  $200^\circ$ , volatilising completely, without melting. Its constitution may be expressed by the

formula,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CNOH} \\ - \text{CO} - \end{array} \text{C}_6\text{H}_4$ .

V. H. V.

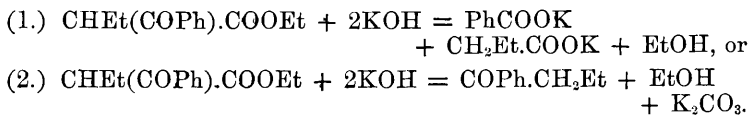
**Derivatives of Benzil.** By B. S. BURTON (*Ber.*, **16**, 2232—2233).—With the view to obtain diphenyltartaric acid, the author has made experiments on the saponification of Zinin's nitril of diphenyltartaric acid,  $\text{C}_{14}\text{H}_{10}\text{O}_2(\text{CHN})_2$ , obtained by the action of anhydrous hydrocyanic acid on an alcoholic solution of benzil (*Annalen*, **34**, 189). The finely powdered nitrile is introduced into a large excess of glacial acetic acid saturated at  $0^\circ$  with hydrobromic acid, and frequently agitated. After some weeks, the unaltered substance is separated, and the clear liquid yields monoclinic crystals of a vitreous lustre. On adding ammonium carbonate to the filtrate, a white precipitate,  $\text{CONH}_2.\text{CPh}(\text{OH}).\text{CPh}(\text{OH}).\text{CONH}_2$ , is produced, insoluble in cold

water, but which can be crystallised from dilute alcohol; it crystallises from hot water in small needles. It softens gradually on heating, begins to darken at  $150^{\circ}$ , becoming completely liquid at  $230^{\circ}$ . Its basic properties are very feeble, as it crystallises unchanged from hot concentrated hydrochloric acid, although it yields a crystalline hydrobromide. It has no acid properties, is not dissolved by sodium carbonate solution, but is soluble in soda solution with decomposition. On boiling it with hydrochloric acid, acid substances are obtained still containing nitrogen. The above mentioned monoclinic crystals consist of the hydrobromide of the amide; this melts at  $185^{\circ}$  with evolution of hydrobromic acid. Sodium carbonate converts it into the amide.

A. K. M.

**Benzoylacetic Acid.** By A. BAEYER and W. H. PERKIN, JUN. (*Ber.*, 16, 2128—2133).—One of the authors has recently shown that ethyl phenylpropionate is converted by sulphuric acid into ethyl benzoylacetate, thus:  $\text{PhC}:\text{C}.\text{COOEt} + \text{H}_2\text{O} = \text{COPh}.\text{CH}_2.\text{COOEt}$  (see *Abstr.*, 1882, 336). The latter is a colourless oil resembling ethyl acetoacetate in odour; when quickly heated, it distils with slight decomposition between  $268$ — $270^{\circ}$ ; it is coloured by ferric chloride. On boiling with water or acids, it is decomposed according to the equation,  $\text{CH}_2\text{Bz}.\text{COOEt} + \text{H}_2\text{O} = \text{PhCOMe} + \text{CO}_2 + \text{EtOH}$ . In order to prepare benzoylacetic acid, a solution of the alkyl salt in soda is left at rest; after filtration, the solution is cooled with ice and carefully acidified, and then exhausted with ether. The acid is obtained from the ethereal extract as a hard crystalline mass, which melts at  $85$ — $90^{\circ}$  with evolution of carbonic anhydride; it is soluble in alcohol and ether, and its solution is coloured violet by ferric chloride.

*Ethylbenzoylacetic acid*,  $\text{CHEtBz}.\text{COOH}$ , is obtained as an ethyl salt by the joint action of sodium and ethyl iodide on ethyl benzoylacetate; on subsequent saponification of this salt, the pure acid is obtained. This latter melts at  $112$ — $115^{\circ}$ , and is generally contaminated by benzoic acid. On boiling the ethyl salt with alcoholic potash, like ethyl acetoacetate, it yields either a mixture of acids, or a ketone, according to the concentration of the alkali, thus:—

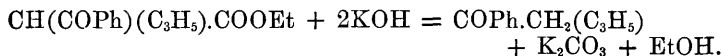


*Diethylbenzoic acid*,  $\text{CEt}_2\text{Bz}.\text{COOH}$ , obtained by a repetition of the process used for the acid above, forms a colourless, crystalline mass melting at  $128$ — $130^{\circ}$ ; when heated with alcoholic potash, it yields diethylacetophenone, boiling at  $230^{\circ}$ , thus:—



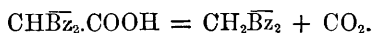
*Allylbenzoylacetic acid*,  $\text{CHBz}(\text{C}_3\text{H}_5).\text{COOH}$ , prepared by the action of allyl iodide on the ethyl salt of sodium benzoylacetic acid, is isomeric with benzoyltetramethylenecarboxylic acid from trimethylene bromide and ethyl benzoylacetate. The former exists as a colour-

less crystalline mass melting at 122—125°, soluble in all menstrua except water; when its ethyl salt is heated with alcoholic potash, it yields allylacetophenone (b. p. 238°), thus:—



*Ethylnitrosobenzoylacetate*,  $\text{COPh}.\text{CNOH}.\text{COOEt}$ , formed by the action of nitrous acid on ethyl benzoylacetate, crystallises in long needles melting at 121°, which dissolve in alkalis to form a golden solution. On long standing in contact with soda, it is converted into an acid,  $\text{COPh}.\text{CH}(\text{OH}).\text{COOH}$ , crystallising in small prisms.

*Dibenzoylactic acid*,  $\text{CH}\overline{\text{Bz}}_2.\text{COOH}$ , obtained by the action of benzoic chloride on ethyl sodium benzoylacetate, and subsequent saponification, crystallises in needles melting at 109°, sparingly soluble in alcohol. This substance on protracted heating with water is converted into *dibenzoylmethane* with evolution of carbonic anhydride, thus:—



This latter compound crystallises in large tables belonging to the rhombic system, which melt at 81° and boil at 200°. By the combined action of sodium and benzoic chloride it is converted into *tribenzoylmethane*,  $\text{CH}\overline{\text{Bz}}_3$ , which crystallises in small needles (m. p. 224°), and sublimes without decomposition.

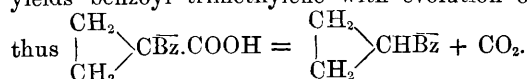
V. H. V.

**Action of Ethylene Bromide on Ethyl Aceto- and Benzoyl-Acetates.** By W. H. PERKIN, JUN. (*Ber.*, 16, 2136—2140).—By the combined action of ethylene bromide and sodium on ethyl acetoacetate, the *ethyl salt of acetyl trimethylene carboxylic acid* is formed according to the equations: I.  $\text{CH}\overline{\text{Ac}}\text{Na}.\text{COOEt} + \text{CH}_2\text{Br}.\text{CH}_2\text{Br} = \text{CH}\overline{\text{Ac}}(\text{C}_2\text{H}_4\text{Br}).\text{COOEt} + \text{NaBr}$ ; and II.  $\text{C}\overline{\text{Ac}}\text{Na}(\text{C}_2\text{H}_4\text{Br}).\text{COOEt} = \text{CH}_2 \begin{array}{l} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} \text{C}\overline{\text{Ac}}.\text{COOEt} + \text{NaBr}.$

This substance is a colourless oil boiling at 193—195°, and yields the corresponding acid as a thick oil on saponification and subsequently acidifying the alkali salt. The silver salt crystallises in characteristic warty masses.

Similarly, *benzoyl trimethylene carboxylic acid*,  $\text{CH}_2 \begin{array}{l} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} \text{C}\overline{\text{Bz}}.\text{COOH}$ ,

may be obtained; it crystallises in the monoclinic system, and melts at 148° with evolution of carbonic anhydride. Its *silver* salt forms a white flocculent precipitate, the *ethyl* salt a colourless oil boiling at 280—283°. Benzoyl trimethylene carboxylic acid when heated to 200° yields benzoyl trimethylene with evolution of carbonic anhydride,

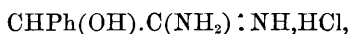


The author is engaged in investigating homologues of the substances above described.

V. H. V.

**Phenylhydroxyacetimidoether and Amidine.** By C. BEYER (*J. pr. Chem.* [2], **28**, 190—191).—Benzaldehyde cyanhydrin is dissolved in ether, 1 mol. proportion of alcohol added, and a stream of dry hydrochloric acid passed into the liquid. The resulting *hydrochloride*,  $\text{CHPh(OH).C(OEt):NH.HCl}$ , crystallises in needles, melts at  $121^\circ$ , and on treatment with potash and ether, yields *phenylhydroxyimidoether*,  $\text{CHPh(OH).C(OEt):NH}$ , crystallising in fine needles and melting at  $71\text{--}72^\circ$ . On strongly heating the hydrochloride, it is resolved into ethyl chloride and mandelamide; on treatment with water, it yields *ethyl mandelate*,  $\text{CHPh(OH).COOEt}$ , as a heavy colourless liquid of faint jasmine-like odour, boiling at  $253\text{--}255^\circ$ , and solidifying to a crystalline mass in a freezing mixture.

By the action of alcoholic ammonia on the imidoether hydrochloride, the corresponding *phenylhydroxyamidine hydrochloride*,



was obtained crystallised in fine prisms, melting at  $213\text{--}214^\circ$ . The free amidine could only be obtained in an impure state, and then formed stellate groups of needles having a strongly alkaline reaction and melting at  $110^\circ$ .  
A. J. G.

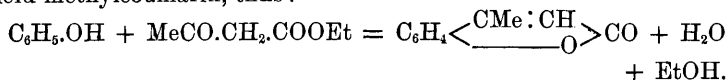
**Derivatives of Orthonitrocinnamic Acid.** By A. EINHORN (*Ber.*, **16**, 2208—2216).—*Orthonitrophenyl- $\beta$ -bromopropionic acid*,  $\text{NO}_2\text{.C}_6\text{H}_4\text{.CHBr.CH}_2\text{.COOH}$ , is prepared by heating orthonitrocinnamic acid (10 grams) with a solution of hydrobromic acid in glacial acetic acid (100 grams) saturated at  $0^\circ$ . The mixture is heated in a sealed tube for about half an hour on a water-bath, and frequently shaken until the nitro-acid is dissolved. The product is purified by boiling it with benzene and recrystallising from chloroform; it forms pale yellow monoclinic crystals melting at  $139\text{--}140^\circ$ , with decomposition. It dissolves readily in the ordinary solvents, but is only sparingly soluble in benzene. It dissolves to a small extent in warm water, decomposition however taking place with formation of indoxyl. Boiling concentrated sulphuric acid is almost without action on it, whilst alkalis very readily decompose it. On treating the powdered acid with an excess of cold sodium carbonate solution, a clear solution is obtained, which soon assumes a bright red colour, whilst a precipitate forms which the author assumes to be the *lactone* of orthonitrophenyl- $\beta$ -lactic acid,  $\text{NO}_2\text{.C}_6\text{H}_4\text{.CH} \begin{smallmatrix} \text{CH}_2 \\ \text{---O---} \end{smallmatrix} \text{CO}$ . The filtrate contains small quantities of orthonitrocinnamic acid, orthonitrophenyl- $\beta$ -lactic acid, and orthonitrostyrene. The lactone is readily soluble in chloroform, acetone, benzene, and glacial acetic acid, sparingly in ether and in absolute alcohol, whilst alkalis convert it into the corresponding hydroxy-acid. It is converted into orthonitrostyrene and carbonic anhydride by boiling with water, some indoxyl, indigo, and probably also orthonitrophenyl- $\beta$ -lactic acid being simultaneously produced. Indigo is also formed when it is boiled with glacial acetic acid or acetic anhydride. By the action of zinc-dust and hydrochloric acid on a solution of the nitro-lactone in glacial acetic acid, hydrocarbo-



styril is formed, and not the expected amido-lactone. When finely powdered orthonitrophenyl- $\beta$ -bromopropionic acid is added to a hot solution of sodium carbonate and the product steam distilled, an oil is obtained solidifying in a freezing mixture to a white crystalline mass, which melts at about 12—13.5°. When *orthonitrostyrene*,  $C_8H_7NO_2$ , is heated with concentrated sulphuric acid, it assumes a blue colour. On adding a solution of bromine in chloroform to nitrostyrene also dissolved in chloroform, the liquid being kept cool with ice, *orthonitrostyrene dibromide*,  $NO_2.C_6H_4.CHBr.CH_2Br$ , is obtained, melting at 52° and volatile in steam. Besides nitrostyrene (10 per cent.), *orthonitrocinnamic acid* (16 per cent.), and *orthonitrophenyl- $\beta$ -lactic acid* (42 per cent.), are formed in the above reaction, and the latter compound can also be obtained by warming the lactone with baryta-water. The purified acid,  $NO_2.C_6H_4.CH(OH).CH_2.COOH$ , is readily soluble in alcohol and in water, crystallising from the latter in six-sided monoclinic prisms, melting at 126°. When heated with dilute sulphuric acid at 190°, it yields *orthonitrocinnamic acid*; with concentrated sulphuric acid it yields *indoin*. The *methyl derivative* melts at 51°; the *barium salt*,  $(C_8H_6NO_5)_2Ba + 2H_2O$ , crystallises in needles. A direct comparison of this acid, with that obtained by Baeyer and Drewson (p. 59), shows that the two are identical.

A. K. M.

**Substituted Coumarins.** By H. v. PECHMANN and C. DUISBERG (*Ber.*, 16, 2119—2128).—The ethyl salts of aceto- and benzoyl-acetic acids react with the phenols in presence of a dehydrating agent to form substituted coumarins or hydroxycoumarins. Thus, for example, phenol and ethyl acetoacetate, in presence of strong sulphuric acid, yield methylcoumarin, thus:



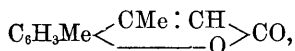
In this communication a description is given of the preparation and properties of various substituted coumarins obtained by means of this general method.

*$\beta$ -Methylumbelliferone*,  $OH.C_6H_3 < \frac{CMe:CH}{O} > CO$ , from resorcinol and ethyl acetoacetate, crystallises in prisms or needles melting at 185°, insoluble in water, soluble in alcohol and in ammonia and caustic alkalis. Its solutions are of a pale yellow colour, and display a characteristic blue fluorescence. When heated with potash, it yields resacetophenone and also resorcinol, and in this connection the author mentions that traces of resorcinol can be detected by the fluorescence formed on adding ethyl acetoacetate and sulphuric acid to the suspected solution. The resacetophenone,  $C_6H_3(OH)_2.COMe$ , is identical with the substance obtained by Nencki and Sieber from resorcinol and acetic acid. The *acetyl* and *benzoyl* derivatives of  $\beta$ -methylumbelliferone crystallise in needles, soluble in alcohol, sparingly soluble in water and ether; the former melts at 150°, the latter at 160°.

The *methyl-ether* of  $\beta$ -methylumbelliferone is a crystalline substance

(m. p. 159°), resembling in all its properties the corresponding hydroxyl-compound mentioned above; when heated with potash, it is converted into a *carboxyl-acid*,  $C_6H_3(OMe)(OH).CMe:CH.COOH$ , crystallising in four-sided tables, which melt at 140° with evolution of carbonic anhydride, and are insoluble in water, easily soluble in alcohol. *Dimethyl-β-resorcylic acid*,  $C_6H_3(OMe)_2.COOH$ , obtained by further methylation and subsequent oxidation of the above-mentioned methyl-ether, crystallises in white needles (m. p. 108°).

*β-Phenylumbelliferone*,  $C_6H_3(OH)<\frac{CPh:CH}{O}>CO$ , from resorcinol and ethyl benzoylacetate, crystallises in colourless leaflets melting at 244°; *αβ-dimethylumbelliferone*,  $C_6H_3(OH)<\frac{CMe:CMe}{O}>CO$ , from resorcinol and ethyl dimethylacetoacetate in colourless needles melting at 256°; *β-methylcoumarin* from phenol and ethyl acetoacetate in colourless needles; *meta-toluene-β-methylcoumarin*,

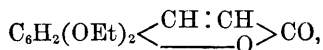


from paracresol and ethyl acetoacetate in large refracting needles; *dihydroxymethylcoumarin*,  $C_6H_2(OH)_2<\frac{CMe:CH}{O}>CO$ , in colourless needles (m. p. 235°). The solutions of all these substances, with the exception of the last named, display a well-marked blue fluorescence.

V. H. V.

**Æsculetin.** By W. WILL (*Ber.*, 16, 2106—2119).—The author, associated with Tiemann, has shown that dimethylæsculetin resembles in many points methylumbelliferone and coumarin (*Abstr.*, 1882, 199). As the former has been recognised to be a monhydroxyl-derivative of coumarin, it becomes exceedingly probable that æsculetin is a dihydroxyl-derivative. In order to obtain further evidence in support of this conjecture, the author has repeated with æsculetin Perkin's researches on coumarin (this *Journal*, *Trans.*, 1881, 409), and proves that the former undergoes transformation precisely similar to the latter, yielding isomeric *α*- and *β*-æsculetic acids, related to one another as the *α*- and *β*-orthomethoxyphenylacrylic acids.

*Monethylæsculetin*,  $\frac{OEt}{OH}>C_6H_2<\frac{CH:CH}{O}>CO$ , is obtained, together with the di-derivative, by heating æsculetin with solid potash and ethyl iodide in alcoholic solution; the two products may be separated by ether which dissolves the di-derivative. Monethylæsculetin forms more or less colourless crystals (m. p. 143°), soluble in dilute alkalis; its solutions give a blue fluorescence. *Diethylæsculetin*,



crystallises in glistening leaflets (m. p. 109°), sparingly soluble in water, readily soluble in ether and benzene. It dissolves in hot soda, forming a red solution, from which the sodium compound separates

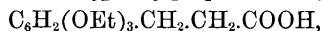
out on evaporation. If the residue be digested with ethyl iodide, there is formed the *ethyl salt of  $\beta$ -triethylæsculetic acid*,



This substance crystallises in glistening tablets melting at  $75^\circ$ , boiling at  $360^\circ$ , insoluble in water, readily soluble in dilute acids and alkalis; on saponification it is converted into  $\beta$ -triethylæsculetic acid,



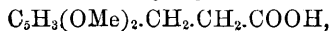
This acid forms colourless glistening prisms melting at  $144^\circ$ ; a solution of its ammonium salt gives precipitates with salts of lead, mercury, copper, and silver. If in the preparation of the ethyl salt of  $\beta$ -triethylæsculetic acid an excess of ethyl iodide be avoided, and the time of heating be not more than 4—5 hours, the *ethyl salt of the isomeric  $\alpha$ -acid* is produced. It forms thick golden prisms melting at  $51^\circ$ , boiling at  $230^\circ$ , insoluble in water, soluble in alcohol and ether; when heated to its boiling point it is transformed into the isomeric  $\beta$ -compound.  *$\alpha$ -Triethylæsculetic acid* can be obtained by the saponification of the corresponding ethyl salt; it is a crystalline substance melting at  $102^\circ$ , and a solution of its ammonium salt gives precipitates with salts of lead, zinc, copper, and mercury. When heated to its boiling point or with hydrochloric acid, it is converted into the isomeric  $\beta$ -acid. On reduction with sodium-amalgam, both the  $\alpha$ - and  $\beta$ -triethylæsculetic acids yield the same *triethoxyphenylpropionic acid*,



which crystallises in leaflets melting at  $77^\circ$ ; a solution of its ammonium salt gives precipitates with salts of lead, silver, mercury, and copper.  $\alpha$ - and  $\beta$ -triethylæsculetic acids are converted by oxidation with alkaline permanganate in the cold into the same triethoxybenzaldehyde,  $\text{C}_6\text{H}_2(\text{OEt})_3\text{CHO}$ , forming colourless crystals melting at  $95^\circ$ , insoluble in water, soluble in alcohol and ether. It has all the characteristic properties of an aldehyde. If the oxidation of the triethylæsculetic acid be effected at  $60^\circ$  instead of the aldehyde, *triethoxybenzoic acid*,  $\text{C}_6\text{H}_2(\text{OEt})_3\text{COOH}$ , is obtained: this substance crystallises in delicate needles melting at  $134^\circ$ , and solution of its ammonium salt gives precipitates with salts of lead, mercury, and silver. On distilling the potassium salt of this acid with potash, it is converted into a substance crystallising in needles melting at  $57^\circ$ , which gives the characteristic phloroglucol reaction with ferric chloride. From want of material the author was unable to examine the compound more fully.

*$\alpha$ -Dimethylumbellic acid*,  $\text{C}_6\text{H}_3(\text{OMe})_2\text{CH}:\text{CH}.\text{COOH}$ , obtained by heating 1 mol. methylumbelliferone with 1 mol. of sodium dissolved in methyl alcohol, and 1 mol. methyl iodide, crystallises in colourless needles melting at  $138^\circ$ , soluble in alcohol, ether, and benzene. On boiling with hydrochloric acid, it is converted into the more stable isomeric compound.

Both  $\alpha$ - and  $\beta$ -dimethylumbellic acids when reduced by sodium-amalgam yield the same *dimethoxypropionic acid*,



which forms a white crystalline powder melting at  $105^{\circ}$ ; its ammonium salts give precipitates with salts of silver, lead, and mercury.  $\alpha$ -Dimethylumbellic acid is converted by oxidation into a dimethoxybenzoic acid,  $C_6H_3(OMe)_2.COOH$ , identical with the  $\beta$ -dimethylresorcylic acid,  $C_6H_3(OMe)_2.COOH$  [ $COOH : OMe : OMe = 1 : 2 : 4$ ], obtained by the oxidation of the corresponding aldehyde.

Bromine acts readily on diethylæsculetin dissolved in carbon bisulphide to form monobromdiethylæsculetin,  $C_{13}H_{13}O_4Br$ , a crystalline substance melting at  $169^{\circ}$ , and converted on boiling with concentrated alcoholic potash into diethoxycoumarilic acid,  $C_{13}H_{14}O_5$ , which crystallises in delicate transparent needles melting at  $195^{\circ}$ . On reduction with sodium-amalgam, it is converted into a substance probably homologous with hydrocoumarilic acid.

V. H. V.

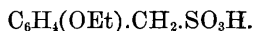
**Benzylsulphonic Acid.** By G. MOHR (*Annalen*, **221**, 215—229).—*Nitrobenzylsulphonic acid*,  $C_6H_4(NO_2).CH_2.SO_3H$ , prepared by the method described by Böhler (*Annalen*, **154**, 50; *Ber.*, **5**, 688), yields a chloride which is decomposed by heat into sulphurous oxide, and paranitrobenzyl chloride (m. p.  $71.5^{\circ}$ ) mixed with a small quantity of the ortho-compound. On reducing an ammoniacal solution of the nitrobenzylsulphonic acid with sulphuretted hydrogen, *paramidobenzylsulphonic acid*,  $C_6H_4(NH_2).CH_2.SO_3H$ , is deposited in colourless needles. The mother-liquor contains a mixture of the para- and ortho-compounds. The para-acid is sparingly soluble in cold water; 100 grams of the solution at  $11^{\circ}$  contain 0.097 gram acid. The salts are crystalline, and freely soluble in water. The *diazo-compound*,

$C_6H_4 \begin{array}{c} \text{---N} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{SO}_3 \end{array} \text{N}$ , is prepared by passing nitrous acid into the amido-

acid suspended in water. As soon as an evolution of nitrogen is observed, the mixture is filtered. On adding alcohol to the filtrate, the diazo-compound is obtained in colourless microscopic crystals. When boiled with water it is decomposed, yielding parahydroxybenzylsulphonic acid,  $C_6H_4(OH).CH_2.SO_3H$ , which crystallises in deliquescent needles, freely soluble in alcohol. The solution of the acid or of its salts gives with ferric chloride a blue coloration, which is destroyed by alcohol. The potassium and the barium salts crystallise in prisms soluble in water. The former contains 0.5, and the latter 7.5 mols.  $H_2O$ .

By the action of hydrobromic acid on the diazo-compound, *para-bromobenzylsulphonic acid*,  $C_6H_4Br.CH_2.SO_3H$ , is obtained as a syrupy liquid. The *barium* salt,  $(C_6H_4Br.CH_2.SO_3)_2Ba + 1\frac{1}{2}H_2O$ , forms colourless plates, soluble in water. The *chloride* (m. p.  $107^{\circ}$ ) is soluble in benzene and ether.

The diazo-compound is decomposed by absolute alcohol under pressure, yielding *paraethoxybenzylsulphonic acid*,



The barium salt of this acid crystallises with 2 mols.  $H_2O$ .

*Parazobenzylidisulphonic acid*,  $C_6H_4(CH_2.SO_3H).N_2.C_6H_4.CH_2.SO_3H$ ,

prepared by the oxidation of amidobenzylsulphonic acid with potassium permanganate, forms the following salts:  $C_{14}H_{12}N_2S_2O_6K_2 + 1\frac{1}{2}H_2O$ , orange-coloured plates, soluble in water;  $C_{14}H_{12}N_2S_2O_6Ba + 1\frac{1}{2}H_2O$ , yellow needles, sparingly soluble;  $C_{14}H_{12}N_2S_2O_6Ag_2 \cdot 2H_2O$ , yellow needles, soluble in hot water. The *chloride* forms crystalline leaves melting at  $149^\circ$ , soluble in benzene.

Nitrobenzylsulphonic acid is converted into the dinitro-acid by the action of a mixture of strong sulphuric and nitric acids. The anhydrous potassium salt, and the lead and barium salts containing 4 mols.  $H_2O$ , are soluble in water. *Amidonitrobenzylsulphonic acid* is sparingly soluble in cold water. The *potassium salt* forms purple anhydrous crystals, and the *barium salt*,  $[C_6H_3(NH_2)(NO_2)CH_2SO_3]_2Ba \cdot 2H_2O$ , yellow needles or plates.

*Diamidobenzylsulphonic acid*,  $C_6H_3(NH_2)_2 \cdot CH_2 \cdot SO_3H$ , crystallises in colourless needles, soluble in acids or alkalis. The ammoniacal solution gives, with silver nitrate, a white precipitate which rapidly turns black.

W. C. W.

**Parabromotoluenedisulphonic Acid.** By O. KORNATZKI (*Annalen*, **221**, 191—202).—*Parabromotoluenedisulphonic acid*, prepared by passing sulphuric anhydride into a solution of bromotoluene in sulphuric acid, forms a deliquescent crystalline mass.

The *potassium salt*,  $C_7H_5Br(SO_3K)_2 + H_2O$ , crystallises in colourless needles or rhombic prisms, which dissolve freely in cold water. The *barium salt*,  $C_7H_5BrS_2O_6Ba + 5H_2O$ , forms colourless prisms, needles, or plates, soluble in hot water, and the *lead salt*,  $C_7H_5BrS_2O_6Pb + 2H_2O$ , crystallises in colourless needles, which dissolve easily in water. The *chloride*,  $C_7H_5Br(SO_2Cl)_2$ , is deposited from an ethereal solution in colourless rhombic plates melting at  $99^\circ$ . The *amide* is sparingly soluble in water and alcohol. It melts above  $260^\circ$ .

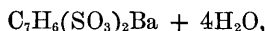
*Parabromotoluenedisulphonic acid* is slowly attacked by strong nitric acid with the formation of sulphuric, dibromonitrotoluenedisulphonic, nitrotoluenedisulphonic, and bromodisulphobenzoic acids.

*Potassium parabromodisulphobenzoate*,  $C_6H_2Br(COOK)(SO_3K)_2 + H_2O$ , forms colourless plates, soluble in water. The *barium salt* crystallises in plates containing 12 mols.  $H_2O$ . The *chloride* is deposited from an ethereal solution in rhombic plates melting at  $151^\circ$ . The *amide* crystallises in prisms soluble in ammonia and in warm water. It melts above  $250^\circ$ .

*Potassium dibromonitrotoluenedisulphonate*,  $C_7H_4Br_2(NO)_2SO_3K + H_2O$ , is soluble in alcohol and water. The *barium salt* forms thin plates, containing  $3\frac{1}{2}$  mols.  $H_2O$ .

*Potassium nitrotoluenedisulphonate*,  $C_7H_5NO_2(SO_3K)_2$ , crystallises in thin needles, soluble in warm water. The *amidotoluenedisulphonic acid*, obtained by the action of ammonium sulphide on this salt, is not identical with either of the amido-acids described by Pechmann (*Annalen*, **173**, 217), or Lorenz (*ibid.*, **172**, 188). It forms yellow needles or prisms, which dissolve freely in water. The *toluenedisulphonic acid*, which is formed by the reduction of sodium parabromotoluenedisulphonate, is not identical with any of the toluenedisulphonic acids described by Blomstrand and Hakansson (*Ber.*, **5**, 1084),

Claesson and Berg (*ibid.*, **13**, 1170), or Senhofer (*Annalen*, **164**, 126). It yields an anhydrous potassium salt, and a barium salt,



both of which are very soluble in water. The *chloride* crystallises in prisms melting at  $86.5^\circ$ , soluble in ether and light petroleum, and the *amide* forms colourless needles which melt above  $260^\circ$ .

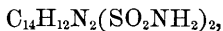
W. C. W.

**Azotoluenedisulphonic Acids.** By O. KORNATZKI (*Annalen*, **221**, 179—191).—The author finds that the only satisfactory general method of preparing azotoluenesulphonic acids is by the oxidation of the potassium salt of the amido-acids.

*Orthazotoluenediparasulphonic acid*, and *parazotoluenediorthosulphonic acid*, which Neale (*Annalen*, **203**, 73) prepared by reducing the corresponding nitrotoluenesulphonic acids with zinc-dust and potash solution, are also formed by the action of potassium permanganate on orthamidotolueneparasulphonic acid (described by Hayduck, *Annalen*, **172**, 204), and on paramidotoluenearthosulphonic acid.

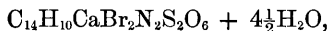
*Parazotoluenedimetasulphonic acid*, obtained by a similar reaction from the corresponding amido-acid (*ibid.*, **173**, 195) yields a *barium* salt,  $\text{C}_{14}\text{H}_{12}\text{BaN}_2\text{S}_2\text{O}_6 + 3\text{H}_2\text{O}$ , which forms small red crystals, sparingly soluble in water.

*Orthazotoluenedimetasulphonic acid* crystallises in plates of a red colour, which dissolve freely in alcohol or water. The *potassium* salt,  $\text{C}_{14}\text{H}_{12}\text{K}_2\text{N}_2\text{S}_2\text{O}_6$ , also forms beautiful red-coloured plates, soluble in warm water. The *barium* salt,  $\text{C}_{14}\text{H}_{12}\text{BaN}_2\text{S}_2\text{O}_6 + \text{H}_2\text{O}$ , forms sparingly soluble microscopic plates, which effloresce on exposure to the air. The *calcium* salt crystallises in microscopic needles containing 3 mols.  $\text{H}_2\text{O}$ . The *lead* salt,  $\text{C}_{14}\text{H}_{12}\text{PbN}_2\text{S}_2\text{O}_6 + \text{H}_2\text{O}$ , is deposited from a solution in hot nitric acid, in needles which effloresce in the air. The *chloride*,  $\text{C}_{14}\text{H}_{12}\text{N}_2(\text{SO}_2\text{Cl})_2$ , crystallises in dark red needles melting at  $218^\circ$ , soluble in benzene. The *amide*,



forms rhombic plates which melt at  $250^\circ$ , and are soluble in ammonia.

Dibromoparamidotoluenearthosulphonic acid, described by Jenssen (*ibid.*, **172**, 234) is slowly converted into *dibromazotoluenedisulphonic acid* by oxidation with potassium permanganate. The *azo-acid* crystallises in glistening red plates which dissolve freely in water. The *potassium* salt,  $\text{C}_{14}\text{H}_{10}\text{K}_2\text{Br}_2\text{N}_2\text{S}_2\text{O}_6 + 4\text{H}_2\text{O}$ , forms six-sided plates, soluble in hot water. The orange-coloured *barium* salt,  $\text{C}_{14}\text{H}_{10}\text{BaBr}_2\text{N}_2\text{S}_2\text{O}_6 + 5\text{H}_2\text{O}$ , and the red *calcium* salt,



forms microscopic plates, sparingly soluble in hot water. The *lead* salt is deposited from hot dilute nitric acid in beautiful rhombic prisms containing 5 mols.  $\text{H}_2\text{O}$ . The *chloride*,  $\text{C}_{14}\text{H}_{10}\text{Br}_2\text{N}_2(\text{SO}_2\text{Cl})_2$ , crystallises from benzene in pale red prisms melting at  $226^\circ$ . The *amide* melts at  $260^\circ$ .

*Tetrabromorthoazotoluenediparasulphonic acid*, prepared from Hayduck's dibromamidotoluenesulphonic acid (*ibid.*, 172, 211), forms glistening red plates, which dissolve easily in water and alcohol. The *potassium* salt forms microscopic plates, containing 2 mols.  $\text{H}_2\text{O}$ . It is sparingly soluble. The *barium* salt,  $\text{C}_{14}\text{H}_8\text{BaBr}_4\text{N}_2\text{S}_2\text{O}_6 + 9\text{H}_2\text{O}$ , crystallises in six-sided plates, which are sparingly soluble in hot water. The *calcium* salt,  $\text{C}_{14}\text{H}_8\text{CaBr}_4\text{N}_2\text{S}_2\text{O}_6 + 8\text{H}_2\text{O}$ , and the *lead* salt,  $\text{C}_{14}\text{H}_8\text{PbBr}_4\text{N}_2\text{S}_2\text{O}_6 + 9\text{H}_2\text{O}$ , form red-coloured plates. The *chloride*,  $\text{C}_{14}\text{H}_8\text{Br}_4\text{N}_2(\text{SO}_2\text{Cl})_2$ , is deposited from benzene in dark red plates, which melt at  $243^\circ$  with decomposition.

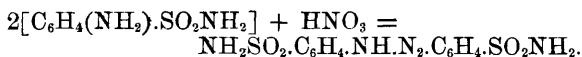
A hydrazo-acid is not produced by the action of stannous chloride on the potassium salt. W. C. W.

**Amidobenzenemetasulphonamide.** By F. HYBBENETH (*Annalen*, 221, 204—208).—The preparation of *amidobenzenemetasulphonamide*,  $\text{C}_6\text{H}_4(\text{NH}_2).\text{SO}_2\text{NH}_2$  (m. p.  $142^\circ$ ), has been previously described (*Annalen*, 172, 72). The oxalate, nitrate, and hydrochloride are crystalline. When nitrous acid is passed into a mixture of absolute alcohol and the sulphonamide, an orange-coloured diazo-compound is produced. If nitric acid is substituted for alcohol, either an orange-coloured powder soluble in water, or a yellow crystalline compound, will be obtained. The orange-coloured substance has the composition  $\text{C}_6\text{H}_4(\text{SO}_2\text{NH}_2).\text{N}_2.\text{NO}_3$ . It is decomposed by boiling with water or alcohol, yielding nitrogen and benzenesulphonamide (m. p.  $156^\circ$ ).

The yellow crystalline compound



previously mentioned, is insoluble in water. It melts at  $183^\circ$  with decomposition. It is decomposed by hydrochloric acid, yielding chlorobenzenesulphonamide (m. p.  $148^\circ$ ), which was first prepared by Kieselinsky (*Annalen*, 180, 110).



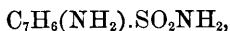
The conditions which determine the formation of either of the two compounds have not yet been ascertained. W. C. W.

**Orthamidotolueneparasulphonamide.** By W. PAYSAN (*Annalen*, 221, 210—215).—The amide of orthamidotolueneparasulphonic acid,  $\text{NH}_2.\text{C}_6\text{H}_3\text{Me}.\text{SO}_2\text{NH}_2$ , prepared by the action of sulphuretted hydrogen on an ammoniacal solution of orthonitrotolueneparasulphonamide (m. p.  $128^\circ$ ), crystallises in four-sided prisms melting at  $175^\circ$ , which are sparingly soluble in cold water or alcohol. It forms a series of crystalline salts.

The *diazo*-compound,  $\text{NH}_2\text{SO}_2.\text{C}_6\text{H}_3\text{Me}.\text{N}_2.\text{NHC}_6\text{H}_3\text{Me}.\text{SO}_2\text{NH}_2$ , is obtained as a pale-yellow powder, when nitrous acid is passed into a mixture of the sulphonamide and alcohol. It detonates feebly when heated, and is also easily decomposed by dilute acids, *e.g.*, by hydrochloric acid, it is split up into nitrogen, amidotoluenesulphonamidehydrochloride and orthochlorotolueneparasulphonamide,  $\text{C}_6\text{H}_3\text{MeCl}.\text{SO}_2\text{NH}_2$

(m. p. 135°). The latter compound crystallises in white needles or plates, which are sparingly soluble in water. By the action of hydrochloric acid at 150°, it is converted into orthochlorotolueneparasulphonic acid. The acid exists as an oily liquid. Its potassium and barium salts do not contain water of crystallisation. The chloride is also an oily liquid. When nitrous acid is passed into orthamidotolueneparasulphonamide, made into a paste with nitric acid, an exceedingly unstable colourless diazo-compound is produced, which is decomposed by boiling alcohol, yielding the ethyloxidtoluenesulphonic acid described by Hayduck (*Annalen*, **172**, 215). W. C. W.

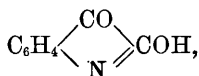
**Paramidotolueneorthosulphonamide.** By A. HEFFTER (*Annalen*, **221**, 208—210).—*Paramidotolueneorthosulphonamide*,



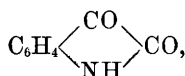
is obtained by the action of sulphuretted hydrogen on a warm ammoniacal solution of paranitrotoluenesulphonamide (*Annalen*, **172**, 233). It crystallises in silky needles or plates which melt at 164°, and dissolve in alcohol or warm water. It forms a crystalline nitrate, oxalate, and hydrochloride. When nitrous acid is passed into an alcoholic solution of the sulphonamide, a yellow amorphous compound is produced, which is decomposed by hot absolute alcohol, yielding the amide of tolueneorthosulphonic acid (m. p. 154°), which has been described by Claesson and Wallin (*Ber.*, **12**, 1850). A diazo-derivative of amidotoluenesulphonamide could not be isolated. *Parachlorotolueneorthosulphonamide* (m. p. 138°) is produced when nitrous acid acts on the sulphonamide in presence of hydrochloric acid. The  $\text{SO}_2$ -group in paramidotoluenesulphonamide is not eliminated by oxidation with potassium permanganate; but the amide of azotoluenedisulphonic acid (m. p. 270°), described by Neale (*Annalen*, **203**, 52), is formed.

W. C. W.

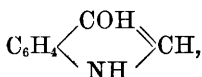
**Compounds of the Indigo-group.** By A. BAEYER (*Ber.*, **16**, 2188—2204).—Part IV.—The author has finally established the position of the hydrogen-atom (external to the benzene-ring) in indigo, showing that the latter is an imido-body, produced by the union of two indogen-groups. In the conversion of isatin and indoxyl into members of the true indigo-group, an isomeric change takes place, *pseudoisatin* and *pseudoindoxyl* existing however only in combination :



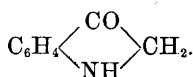
Isatin.



Pseudoisatin.



Indoxyl.



Pseudoindoxyl.

For the stability of pseudoisatin it is sufficient to replace the hydrogen of the  $\text{NH}$ -group by a monad radicle, whilst in the case of



pseudoindoxyl, a dyad-group must replace both hydrogen-atoms of the group  $\text{CH}_2$ .

*Action of Nitrous Acid on Indoxyl and Indoxyl-compounds.*—On treating a solution of indoxyl with sodium nitrite and then acidifying, slender yellowish needles separate which, from their similarity to the nitrosamine of ethylindoxyl (obtained in the same way), and from their behaviour to hydrochloric acid, must be the *nitrosamine of indoxyl*,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C(OH)} \\ \diagup \quad \diagdown \\ \text{N(ON)} \end{smallmatrix} \text{CH}$ . By the action of indoxyl on diazobenzene hydro-

chloride in dilute aqueous solution, *phenylazoindoxyl*,  $\text{C}_{14}\text{H}_{11}\text{NO}_3$ , separates in very sparingly soluble red needles; it is moderately soluble in alcohol, from which it crystallises in thick orange-coloured prisms of yellowish-green metallic lustre; it melts at  $236^\circ$  with decomposition, and dissolves in warm soda solution, from which it is reprecipitated by carbonic anhydride. Zinc-dust decolorises the alkaline solution, and on exposure to air indigo is formed. *Isonitrosopseudo-*

*indoxyl (pseudoisatin- $\alpha$ -oxime)*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CNOH}$ , was previously described as nitrosoindoxyl (Abstr., 1882, 1102), but an examination of its ethers shows that it is an isonitroso-derivative. The first ether, *pseudoisatin- $\alpha$ -ethylloxime*, is obtained on heating an alcoholic solution of pseudoisatoxime with ethyl iodide and sodium ethylate (1 mol.). It yields isatin on reduction and oxidation, showing that the ethyl-group does not replace the imido-hydrogen; neither can it be derived

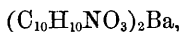
from a nitrosoindoxyl of the formula  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COH} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{C.NO}$ , for it can

be boiled with concentrated hydrochloric acid without undergoing change; nor from  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CHNO}$ , as such a compound, containing ethyl attached to the  $\alpha$ -carbon atom, would not be so readily converted into isatin. Its formula must therefore be  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CNOEt}$ ,

and that of the parent-substance the one given above. This ethyl-derivative is a weak acid, dissolves in alcoholic potash with a violet colour, and in alcoholic sodium ethylate with a blue colour. To prepare the second ether (*ethylpseudoisatin- $\alpha$ -ethylloxime*) an alcoholic solution of pseudoisatoxime, mixed with ethyl iodide and sodium ethylate (1 mol.), is boiled until the sodium salt first formed is completely dissolved, when a quantity (1 mol.) of sodium ethylate and ethyl iodide is added, and the boiling continued for about half an hour; the alcohol is removed by distillation, the product dissolved in ether, and washed with dilute soda solution. It is readily soluble in alcohol and in ether, sparingly in hot water, from which it crystallises in yellow needles melting at  $99^\circ$ ; it is neither attacked by alkalis nor by boiling hydrochloric acid.

Its formula is  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NEt} \end{smallmatrix} \text{CNOEt}$ . Isatoxime and its two ethers, pseudoisatoxime and its first ether, all yield isatin on reduction and subsequent oxidation, whilst the second ether of pseudoisatoxime (containing ethyl attached to nitrogen) yields *ethylpseudoisatin*,

$C_6H_4<\begin{smallmatrix} CO \\ NEt \end{smallmatrix}>CO$ . This crystallises in large blood-red plates melting at  $95^\circ$ , is readily soluble in hot water and in alcohol, less so in ether. It dissolves in alkalis with a yellow colour and formation of ethylisates. Acetylpsuedoisatin behaves in a similar manner, being at once converted into an acetylisate. On acidulating a solution of an ethylisate, ethylpsuedoisatin is at once precipitated, whilst acetylisatic acid is perfectly stable. Barium ethylisate—



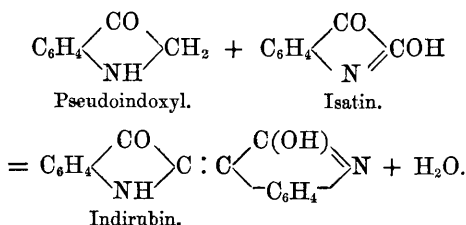
obtained by dissolving ethylpsuedoisatin in warm baryta-water, crystallises in silky yellow needles; the silver salt forms flat yellow needles, moderately soluble in water. Ethylpsuedoisatin yields an indophenin with coal-tar benzene and sulphuric acid, which forms a blue solution with ether (distinction from isatin). Ethylpsuedoisatin, even when heated with concentrated hydrochloric acid for seven hours at  $150$ — $160^\circ$ , is in great part unattacked, whilst ethylisatin is saponified by cold dilute alkalis. By the action of a solution of hydroxylamine hydrochloride and sodium carbonate in dilute alcohol, *ethylpsuedoisatin- $\beta$ -oxime*,  $C_6H_4<\begin{smallmatrix} C(NO)H \\ NEt \end{smallmatrix}>CO$ , is obtained crystallising in yellow four-sided prisms (m. p.  $160$ — $162^\circ$ ). On reduction and subsequent oxidation, it yields ethylpsuedoisatin; it does not yield indigo with ammonium sulphide.

*Action of Aldehydes and Ketonic Acids on Indoxyl.*—On treating an aqueous solution of indoxyl with aldehyde, or with benzaldehyde, and then acidulating with hydrochloric acid, an extremely unstable yellow precipitate is obtained, whilst paranitrobenzaldehyde, terephthalic aldehyde, anthroxanaldehyde, and pyrrocemic acid, when treated in the same way, yield very stable red precipitates. On cautiously heating a mixture of dry indoxylic acid (7 parts) and benzaldehyde (10 parts) carbonic anhydride is evolved; this ceases as soon as the temperature is raised to  $120^\circ$ . When the action is completed, the excess of benzaldehyde is removed by steam-distillation, and the residue crystallised first from alcohol and then from ether. The *indogenide of benzaldehyde* thus obtained crystallises in long, flat, orange-yellow needles, melting at  $175$ — $176^\circ$ . It dissolves readily in alcohol and chloroform, more sparingly in ether, with which it forms a fluorescent solution; it is dissolved by concentrated sulphuric and hydrochloric acids, but is reprecipitated on adding water; it is insoluble in aqueous, but soluble in alcoholic alkalis. Its formation from indoxyl and benzaldehyde takes place thus:  $C_8H_7NO + C_7H_6O = C_{15}H_{11}NO + H_2O$ , similar to the action of nitrous acid on indoxyl, and from the similarity of both products and their behaviour with sodium ethylate, it is evident that they are similarly constituted, and that the formula of the indogenide of benzaldehyde is  $C_6H_4<\begin{smallmatrix} CO \\ NH \end{smallmatrix}>C : CHPh$ . It yields a blue solution with sodium ethylate, showing the indigo-spectrum, the blue colour disappearing on the addition of alcohol. The *indogenide of paranitrobenzaldehyde*,  $C_{15}H_{10}N_2O_3$ , is prepared by adding a solution of paranitrobenzaldehyde in glacial acetic acid to an aqueous

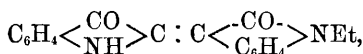
solution of indoxyl acidulated with hydrochloric acid, and then treating the precipitate several times with boiling water, and recrystallising it from acetone. It forms small red needles melting at  $273^{\circ}$ .

The *indogenide of pyroracemic acid*,  $\text{C}_6\text{H}_4\langle\text{CO}\rangle_{\text{NH}}\text{C}:\text{CMe.COOH}$ , is obtained by adding concentrated hydrochloric acid to an aqueous solution of indoxyl and pyroracemic acid, and can be purified by passing a current of air through its solution in ammonia, filtering and precipitating with hydrochloric acid; it crystallises in red needles, and melts at  $197^{\circ}$ . It is readily soluble in acetone and in alcohol, is a strong acid, forms brownish-red solutions with the alkalis and alkaline carbonates, and a blue solution with sulphuric acid. It is reduced by ammonia and zinc-dust, forming a colourless solution, which becomes yellow on exposure to air, and yields a yellow flocculent precipitate on the addition of an acid.

*Action of Isatin and Ethylpseudoisatin on Indoxyl.*—The formation of indirubin from indoxyl and isatin may be compared to the above reactions, in which case indirubin must be regarded as the indogenide of isatin, thus:—



When a hot aqueous solution of indoxyl is poured into a hot solution of ethylisatin mixed with one-fourth its volume of concentrated hydrochloric acid, a violet-coloured liquid is obtained, which yields crystals of the  $\beta$ -*indogenide of ethylpseudoisatin*. It crystallises from boiling alcohol in needles of a coppery lustre, sparingly soluble in acetone, more readily in chloroform. It melts at  $197$ – $198^{\circ}$ , and at higher temperatures volatilises in yellowish-red vapours. The powdered substance is violet, its concentrated solution in chloroform red, and its dilute solution pink, showing a broad band in the middle of the spectrum. It is reduced by zinc-dust and alkalis, yields a brown solution with concentrated sulphuric acid, which changes to violet when heated, and behaves like indigo. From the fact that in the reduction of ethylpseudoisatin, the CO-group next to the benzene nucleus is the one attacked, and also in the reaction with hydroxylamine, it may be assumed that this is also the case in the condensation-product with indoxyl. Its formula is therefore—

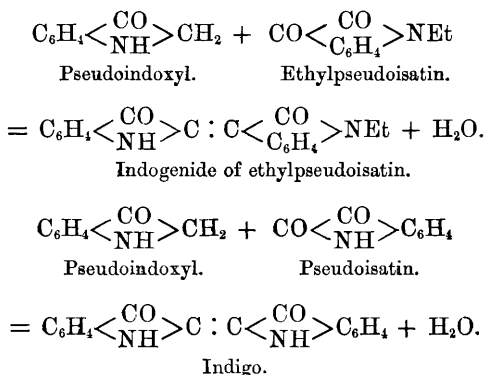


and it is possible that indirubin has a corresponding constitution.

*Diethylindigo.*—Assuming the probability of indigo being an indigo-body, the author attempted to convert ethyl- and benzyl-amidoaceto-

phenone into ethyl- and benzyl-indigo, but without success. By the reduction of the second ether of pseudoisatin- $\alpha$ -oxime by alcoholic ammonium sulphide, *diethylindigo* can be obtained, in which ethyl is attached to the nitrogen, and which still possesses the properties of indigo. It crystallises in blue needles with coppery lustre, it is distinguished from indigo by its moderate solubility in alcohol; but is more sparingly soluble in acetone, chloroform, aniline, ether, and carbon bisulphide. Its solutions are of a pure blue colour, and give an absorption-spectrum very like that of indigo. It forms a greenish-blue solution with concentrated sulphuric acid, which changes to blue on warming (from formation of a sulphonic acid). When heated, it yields purple vapours, condensing in the form of thick blue prisms. With alkalis and zinc-dust, it yields a reduction-compound, and on oxidation, ethylpseudoisatin, proving that the ethyl in diethylindigo is united with nitrogen. In the same way that diethylindigo is obtained from ethylpseudoisatin- $\alpha$ -ethyloxime, indigo can be obtained from pseudoisatin- $\alpha$ -oxime, and also by the action of ammonium sulphide on isatin chloride and on ethylisatin, but from the formulæ of these three indigo-producing substances it will be seen that by their reduction and the splitting off of hydroxylamine, hydrochloric acid, and alcohol respectively, each is capable of yielding an indogen-group or indoxyl.

The constitution of indigo can be adduced from the following considerations:—1. Indigo contains the imido-group; 2. From its formation from diphenyldiacetylene, the carbon-atoms must be arranged thus: Ph.C.C.C.C.Ph; 3. It can only be obtained from such compounds in which the carbon-atom next to the benzene nucleus is also united to oxygen; 4. Its formation and properties show that it is closely related to indirubin and to the indogenide of ethylpseudoisatin; 5. This last substance is formed by the union of the  $\alpha$ -carbon-atom of pseudoindoxyl with the  $\beta$ -carbon-atom of pseudoisatin. Indigo must therefore be the  $\alpha$ -indogenide of pseudoisatin, although from the want of activity of the  $\alpha$ -oxygen-atom in isatin it cannot be directly obtained from indoxyl and isatin.

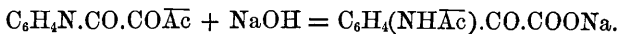


The half molecule ( $\text{C}_8\text{H}_5\text{NO}$ ) of indigo is called by the author

*indogen*, and compounds in which this dyad-group replaces an oxygen-atom, *indogenides*. The indogenides are of a yellow to bluish-red colour, and some of them yield blue salts showing the indigo-spectrum.

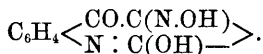
A. K. M.

**Chemical Constitution of Acetylisatin and Acetylisatic Acid.** By H. KOLBE (*J. pr. Chem.* [2], 28, 79—82).—The author objects to the formulæ assigned by Baeyer to isatin and its derivatives; he regards isatin as having the constitution  $C_8H_4N.CO.CO\bar{H}$  (the nitrogen-atom acting as a monovalent element, and replacing one of the hydrogen-atoms in phenyl), and represents the conversion of acetylisatin into sodium acetylisatinate by the equation—



A. J. G.

**Quinisatin.** By A. BAEYER and B. HOMOLKA (*Ber.*, 16, 2216—2221).—Baeyer obtained isatin from oxindole by converting the latter into a nitroso-derivative, then into the amido-derivative which yields isatin on oxidation. The authors have obtained the isatin of quinoline in the same way from  $\gamma$ -hydroxycarbostyryl (*Abstr.*, 1883, 197). To prepare nitroso- $\gamma$ -hydroxycarbostyryl,  $C_9H_6N_2O_3$ ,  $\gamma$ -hydroxycarbostyryl is dissolved in dilute soda solution, a slight excess of sodium nitrite added, and the mixture gradually poured into cold dilute sulphuric acid. The precipitate is washed with water, dried and crystallised from alcohol, when it is obtained in small orange-coloured prisms, sparingly soluble in water, cold alcohol, ether, benzene and chloroform, readily in glacial acetic acid and in hot alcohol. It melts at  $208^\circ$  with decomposition. Alkaline carbonate and ammonia dissolve it, forming a green solution, whilst the fixed alkalis yield reddish-brown solutions. On boiling it with concentrated hydrochloric acid, it decomposes into isatin and hydroxylamine. From its resemblance to isatixime, the authors consider the following constitution probable,



By the action of zinc-dust on its solution in glacial acetic acid, *acetyldihydroxytetrahydroquinoline*,  $C_{11}H_{13}NO_3$ , is obtained, crystallising in long colourless silky needles. When exposed to the air in a moist state, it is rapidly oxidised to a violet-red product, from which the original substance can be obtained by reduction. Acetyldihydroxytetrahydroquinole is very sparingly soluble in cold water, alcohol and ether, moderately in glacial acetic acid, especially on warming; it dissolves in alkali to a violet solution or in excess of the latter to a blue solution, acids reprecipitating it in reddish coloured flocks which gradually become white.

On reducing nitroso- $\gamma$ -hydroxycarbostyryl by means of a saturated solution of stannous chloride in concentrated hydrochloric acid, and subsequently decomposing the tin salt with hydrogen sulphide, a compound of the formula,  $C_9H_7NO_3$ , is obtained, which is probably

$\beta$ - $\gamma$ -dihydroxycarbostyryl,  $C_6H_4 \left\langle \begin{smallmatrix} C(OH):C(OH) \\ N:C(OH) \end{smallmatrix} \right\rangle$ . It crystallises in long colourless needles, very sparingly soluble in water, ether and benzene, readily in alcohol. Heated to  $260^\circ$ , it becomes converted into a brown substance infusible at  $310^\circ$ . With dilute alkalis it yields a blue solution, which becomes decolorised on exposure to the air with formation of a violet precipitate. On adding soda to its solution in alcohol and ether, a deep blue flocculent gelatinous precipitate is produced. When finely powdered  $\beta$ - $\gamma$ -dihydroxycarbostyryl is treated with a solution of ferric chloride in hydrochloric acid at  $70$ – $80^\circ$ , a reddish-yellow liquid is obtained from which *quinisatic acid*,



crystallises out on cooling. It is moderately soluble in cold water, very readily in hot water, from which it crystallises in pale straw-coloured prisms. The *alkali salts* are nearly colourless and readily soluble; the *silver salt* forms a yellowish-green unstable precipitate. On reducing a solution in glacial acetic acid with zinc-dust, and exposing the filtrate to the air, an indigo-blue coloured precipitate is formed, insoluble in water, ether, and chloroform, but soluble in alcohol, the supernatant liquid assuming a green coloration. Both colours are destroyed by acids, but reproduced on adding an alkali. On heating crystallised quinisatic acid for a short time at  $120$ – $125^\circ$  water is given off, and the red anhydride, *quinisatin*,  $C_9H_5NO_3$ , formed: this readily combines with water forming quinisatic acid. It darkens in colour above  $125^\circ$ , melting between  $255^\circ$  and  $260^\circ$ . Soda solution dissolves it to a reddish-yellow solution, which is rapidly decolorised. It forms compounds with aniline and benzene, which are soluble in alkalis, but reprecipitated by carbonic anhydride, showing that quinisatin is not a carboxylic acid. Its formula is pro-

bably either  $C_6H_4 \left\langle \begin{smallmatrix} CO.CO \\ NH.CO \end{smallmatrix} \right\rangle$  or  $C_6H_4 \left\langle \begin{smallmatrix} CO.CO \\ N:C(OH) \end{smallmatrix} \right\rangle$ . A. K. M.

**So-called Pyrocressol.** By H. SCHWARTZ (*Ber.*, **16**, 2141–2145).—In this paper the author mentions that the results of vapour-density determination of the so-called pyrocressol were not in accordance with those obtained in the combustion analyses: the latter corresponded with a formula  $C_{23}H_{26}O_3$ , the former to  $C_{15}H_{14}O$  (comp. *Ber.*, **16**, 1056). Both have been repeated, and the latter formula confirmed; pyrocressol, therefore, may have the constitution of a ditolyl or dibenzyl ketone,  $C_6H_4Me.CO.C_6H_4Me$  or  $CH_2Ph.CO.CH_2Ph$ , although its properties are not in accordance with either of these substances. Similarly, it is shown that the  $\alpha$ -pyrocressol oxide obtained by the oxidation of pyrocressol with chromic acid has the empirical formula  $C_{15}H_{12}O_2$ ; it forms a tetranitro-derivative,  $C_{15}H_8(NO_2)_4O_2$ , crystallising in golden needles, and a tetrabrom-derivative  $C_{15}H_8Br_4O_2$ , crystallising in long white leaflets melting at  $215^\circ$ . V. H. V.

**Derivatives of  $\alpha$ - and  $\beta$ -Naphthol.** By E. FRIEDLÄNDER (*Ber.*, **16**, 2075–2092).—The monohydroxy-phenols readily react with the

monamines yielding the diamines with elimination of water; the best dehydrating agent for effecting this change is calcium chloride, and from the author's experiments it follows that the greatest yield is obtained when 1 mol. of the phenol and 2 mols. of the amine are heated with 1 mol. of calcium chloride. In this communication, the various compounds obtained by the action of aniline and the three toluidines on  $\alpha$ - and  $\beta$ -naphthols are described.

*Phenyl- $\beta$ -naphthylamine*,  $C_{10}H_7.NHPh$ , crystallises in white needles melting at  $108^\circ$ ; *phenyl- $\alpha$ -naphthylamine* in white leaflets melting at  $60^\circ$ .

*Paratolyl- $\beta$ -naphthylamine*,  $C_{10}H_7.NH.C_6H_4$ , forms white glistening leaflets melting at  $102^\circ$ ; its acetyl and benzoyl-derivatives crystallise in needles; with excess of bromine a tetrabrom-compound is obtained, which forms glistening needles melting at  $168^\circ$ . *Paratolyl- $\alpha$ -naphthylamine* forms white prisms melting at  $79^\circ$ ; *orthotolyl- $\alpha$ -naphthylamine* glistening needles melting at  $95^\circ$ . *Orthotolyl- $\beta$ -naphthylamine* crystallises from petroleum in white leaflets melting at  $96^\circ$ ; its *picrate* in reddish-brown needles, and its *benzoyl*-derivative in leaflets.

All the above-mentioned amines give colour-reactions with nitric and chromic acids; when heated with hydrochloric acid they are reconverted into the corresponding phenol and the hydrochloride of the amine.

V. H. V.

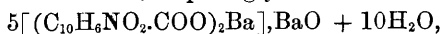
**Naphthalene-derivatives. III.** By F. GRAEFF (*Ber.*, 16, 2246—2255).—The action of nitric acid on naphthonitril takes place in two stages, nitronaphthonitril being first formed, and the CN-group subsequently converted into COOH, so that it is possible to stop the action after the first phase, and obtain nitronaphthonitril. For the nitration of the  $\alpha$ -compound (20 grams) a mixture of 50 c.c. fuming nitric acid, sp. gr. 1.48, with 200 c.c. nitric acid, sp. gr. 1.3, is recommended, whilst for the  $\beta$ -compound 150 c.c. of the stronger acid to 100 c.c. of the weaker acid are employed.  $\alpha$ -Naphthonitril yields three mononitro-derivatives, the chief product melting at  $205^\circ$  as previously stated (*Abstr.*, 1881, 882). Another more soluble nitronaphthonitril melts at  $152$ — $153^\circ$ , whilst the third compound, which has not yet been obtained pure, melts between  $100^\circ$  and  $130^\circ$ . A mononitro-derivative melting at  $172$ — $173^\circ$  is readily obtained from  $\beta$ -naphthonitril, but the chief product melts between  $95^\circ$  and  $120^\circ$ .

*Nitro- $\alpha$ -naphthonitril*,  $C_{10}H_6NO_2.CN$  (m. p.  $152$ — $153^\circ$ ), is more readily soluble in boiling water than its isomeride melting at  $205^\circ$ , very sparingly in light petroleum, more readily in carbon bisulphide, moderately in alcohol and glacial acetic acid, and very readily in benzene and in chloroform. It crystallises in yellowish coloured needles from alcohol, ether, and glacial acetic acid, and in lustrous scales from light petroleum. *Nitro- $\beta$ -naphthonitril* (m. p.  $172$ — $173^\circ$ ) is very sparingly soluble in hot light petroleum, and sparingly in alcohol and glacial acetic acid, from which it separates either in single long crystals of golden lustre or in fern-like clusters; it is moderately soluble in ether and carbon bisulphide, more readily in benzene, and extremely soluble in chloroform. It may be obtained in large nearly white needles of great purity by sublimation. These nitro-

naphthonitrils are saponified by heating them with concentrated hydrochloric acid for five hours at 150—160°.

*Nitro- $\alpha$ -naphthoic acid* (m. p. 241—242°) obtained from the nitro-naphthonitril melting at 205°, is moderately soluble in hot alcohol and glacial acetic acid, less so in ether and chloroform, still more sparingly in benzene and carbon bisulphide, and very sparingly in light petroleum and in water. It crystallises from spirit in flat, concentrically-grouped needles, and sublimes in the form of splendid lustrous scales.

The *potassium salt*,  $C_{10}H_6NO_2.COOK + H_2O$ , forms hard yellowish coloured crystals of a vitreous lustre. On boiling the acid with an excess of barium carbonate, a sparingly soluble *basic salt*,

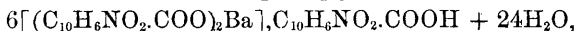


is obtained.

The *silver salt* forms a yellowish amorphous precipitate sparingly soluble in water; the *lead salt* resembles the silver salt and separates from its solution in boiling water in small wart-like forms; the *copper salt* is sparingly soluble in water, from which it separates in small bluish-green crystals; the *methyl-derivative* forms small yellow needles melting at 109—110°, and readily soluble in alcohol; the *ethyl-derivative* is much more sparingly soluble in alcohol, and crystallises in long, slender, well-formed needles melting at 93°; the *isopropyl-derivative* forms lustrous crystals melting at 101·5°, and sparingly soluble in alcohol.

*Nitro- $\alpha$ -naphthoic acid* melting at 255° dissolves readily in most solvents, and sublimes in long colourless needles. For want of material it has not been further examined.

*Nitro- $\beta$ -naphthoic acid* melts at 295°, and in most of its properties resembles the acid melting at 241—242°. It is insoluble in water, sparingly soluble in ether, light petroleum, benzene, chloroform and carbon bisulphide, moderately in hot alcohol and glacial acetic acid; it sublimes in small nearly colourless needles. The *potassium salt*,  $C_{10}H_6NO_2.COOK + H_2O$ , forms small clusters of lustrous needles very readily soluble in water. On boiling the acid with barium carbonate, two salts are obtained, a more sparingly soluble *acid salt*,



crystallising in small lustrous scales, and a more soluble *normal salt* also crystallising in scales. The *methyl-derivative* is sparingly soluble in alcohol, from which it crystallises in clusters of large bright yellow needles, melting at 112°; the *ethyl-derivative* is readily soluble in alcohol, and crystallises in large well-formed dark yellow needles melting at 109°; the *isopropyl-derivative* forms long silky needles melting at 75—76°, and readily soluble in alcohol. This acid appears to be the same as that obtained by Ekstrand (*Ber.*, 12, 1395) from  $\beta$ -naphthoic acid, but which melted at 280° owing to the presence of impurities.

A. K. M.

**Reduction of Dichlorophenanthrone.** By B. LACHOWICZ (*J. pr. Chem.* [2], 28, 168—175).—The preparation and properties of dichlorophenanthrone (phenanthrenedichloroketone) have already been



described by the author (Abstr., 1883, 666). The formation of resinous bye-products is minimised by adding excess of benzene to the phenanthraquinone before running in the phosphoric chloride. Nitric acid readily converts it into the nitro-derivatives of anthraquinone.

*Monochlorophenanthrone*,  $C_{14}H_9OCl$ , is obtained by the reduction of dichlorophenanthrone with iron and acetic acid; it crystallises in large yellow prisms, melts at  $122-123^\circ$ , is readily soluble in alcohol, ether, benzene, light petroleum, &c. It dissolves without decomposition in alkalis, and is not decomposed by long boiling with alcoholic ammonia. By heating with nitric acid of sp. gr. 1.3 it yields *nitrophenanthroquinone*,  $C_{14}H_7NO_4$ , crystallising in orange-yellow plates, melting at  $281-282^\circ$ , and soluble in glacial acetic acid and nitric acid.

*Phenanthrone*,  $C_{14}H_{10}O$ , is obtained by the long-continued action of nascent hydrogen on dichloranthrone, best by gradually adding iron filings to a solution of dichloranthrone in glacial acetic acid heated to  $100-110^\circ$ . Too strong heating leads to the formation of resinous products. It crystallises in brilliant brownish-red tables, melts at  $148-149^\circ$ , resembles the monochloro-derivative in solubilities, and like it, is not decomposed by aqueous alkalis.

The authors consider that phenanthrone has the structural formula  $C_6H_4.CH_2$

$\begin{array}{c} | \\ C_6H_4.CO \end{array}$ , whilst the isomeric compound obtained by Japp and

Streatfeild from ethyl phenanthroxyleneisocrotonate (Trans., 1883,

33) may probably be represented by  $\begin{array}{c} C_6H_4.CH \\ | \\ C_6H_4.CH \end{array} \rangle O$ .

A. J. G.

**Coloured Essential Oils.** By K. HOCK (*Arch. Pharm.* [3], 21, 17—18).—The essential oils of chamomile, wormwood, and millefolium, although differing in colour, were found by the author to have the same absorption-spectrum, namely, three bands in the red and orange. When these oils were submitted to fractional distillation, in each case the portion which distilled at  $260^\circ$  was deep blue, and yielded the same absorption-bands with great distinctness. The blue oils obtained from *Matricaria chamomilla*, *Ferula siumbul*, *Nectandra puchury*, *Inula helenium*, *Pogostemon patschuly*, also by the dry distillation of galbanum, guaiacum, and asafoetida resins, as well as a blue product from oil of valerian, gave the same characteristic absorption-spectrum. From these results, the author concludes that all these blue oils contain the same colouring-matter, *azulene*, which in some cases is present in the plant from which the oil is obtained, in others, is produced by the action of water on some constituent of the plant during distillation, and sometimes is formed by destructive distillation. In the case of those essential oils from which the blue portion was obtained by distillation, an oil oxidised by keeping appeared to yield a larger quantity of the blue product than the same quantity of the fresh oil.

W. R. D.

**Destructive Distillation of Colophony.** By A. RENARD (*Compt. rend.*, **97**, 111—112).—When colophony is introduced into an earthenware retort heated to dull redness it is decomposed, and yields a large quantity of combustible gas rich in hydrogen, and a black, somewhat fluid tar, mixed with a small quantity of water. The tar when distilled at a temperature rising to  $300^{\circ}$  yields a resin which solidifies on cooling, and a liquid which contains benzene and its homologues, a small quantity of naphthalene, and other oils which have not been studied. The residue from the distillation of this liquid is mixed with the resin, and the mixture distilled as far as possible. A residue of coke is left, and an oil was obtained which becomes semi-solid on cooling. This oil contains two isomeric hydrocarbons, *colophanthrenes*, which have the following composition:—

	White.		Yellow.
Carbon .....	93·02	93·20	93·20
Hydrogen .....	7·18	7·01	6·71

The yellow colophanthrene is very slightly soluble in alcohol, from which it separates in yellow crystals with a greenish fluorescence. It boils at about  $360^{\circ}$ , and by repeated crystallisation from alcohol it appears to be converted into the white isomeride. The white colophanthrene is much more soluble in alcohol, from which it is deposited in brilliant white crystals, with a violet fluorescence. It melts at about  $87^{\circ}$ , boils at about  $340^{\circ}$ , and by repeated distillation is partially converted into the yellow isomeride. It also acquires an orange-yellow tint when exposed to light. Both hydrocarbons begin to decompose at the boiling point of sulphur ( $440^{\circ}$ ). When oxidised by chromic acid in acetic acid solution, they both yield carbonic anhydride and a diketone, which yields a sulphonic acid. The potassium salt of this acid when heated in a sealed tube at about  $170^{\circ}$  with a concentrated solution of potassium hydroxide is converted into a deep violet substance; this dissolves in water, and is decomposed by hydrochloric acid, yielding a colouring-matter, which imparts to cotton mordanted with alumina a shade similar to that given by alizarin. C. H. B.

**Extraction of Colouring-matters by a Solution of Borax.** By R. PALM (*Chem. News*, **48**, 114).—For the extraction of alizarin and purpurin from garancin, the author digests the garancin with a cold saturated borax solution until a deep blood-red solution is obtained; this is filtered, and precipitated with sulphuric, hydrochloric, or acetic acid. The precipitate is boiled with a saturated solution of alum, filtered, and cooled; the alizarin and purpurin then deposited are filtered off, and a further quantity of the colouring-matter is precipitated from the filtrate on adding sulphuric acid. The author also employs borax solution for the extraction of santalin from sanders wood, and violet colouring-matter not identical with carmine from cochineal. D. A. L.

**Cochineal Dye-stuffs.** By H. FÜRTH (*Ber.*, **16**, 2169—2171).—By acting on carmine with sulphuric acid, Liebermann and v. Dorp have obtained a brown amorphous dye-stuff, ruficoccine,  $C_{16}H_{10}O_6$ , which on distillation with zinc-dust is converted into an anthracene-like hydrocarbon of composition  $C_{16}H_{12}$  (*Annalen*, **163**, 97). The author has succeeded in obtaining this hydrocarbon not only from coccinine, a quinone derivative of carmine, but also directly from carmine. This hydrocarbon, which condenses in small green-gold leaflets when coccinine or carmine are distilled with zinc-dust, melts at  $186^\circ$ , and is soluble in ether, alcohol, and benzene. By heating acetic chloride and coccinine in sealed tubes at  $100^\circ$ , an acetyl-derivative is obtained, which forms small golden crystals insoluble in water, soluble in alcohol; it cannot be sublimed without decomposition. As coccinine yields a  $C_{16}$  hydrocarbon on distillation, the composition  $C_{14}H_{12}O_5$ , assigned to it by Hlasiwetz and Grabowsky, must be altered to  $C_{16}H_{14}O_5$ , and its acetyl-compound will then be a tetra-derivative,  $C_{16}H_{10}O_2Ac_4$ . Coccinine is thus a tetrahydroxy-quinone,  $C_{16}H_{10}O_2(OH)_2$ , which formula is in accordance with its quinone-like characteristics.

V. H. V.

**Preparation of Diquinoline.** By R. C. TRESSIDER (*Chem. News*, **48**, 31).—Quinoline hydrochloride is heated with an equal weight of zinc chloride at  $350^\circ$  for five or six hours, the flask being fitted with a reflux arrangement. Soda is added to the product until the zinc hydroxide first precipitated is redissolved, the mixture is steam distilled to remove any unchanged quinoline, and the residue which is black and solid is well washed with water, boiled with a large quantity of alcohol, and filtered hot. The filtrate is decolorised with animal charcoal, and again filtered hot: on cooling, diquinoline separates out, and is recrystallised from alcohol. The yield is not large.

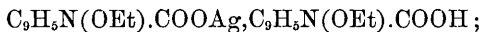
D. A. L.

**Hydroxycinchonic Acid.** By W. KÖNIGS and G. KÖRNER (*Ber.*, **16**, 2152—2160).—By fusing cinchonic acid with potash, one of the authors has obtained a hydroxycinchonic acid,  $C_9H_8N(OH).COOH$  (*Abstr.*, 1879, 472); this acid is converted into a chloro-derivative,  $C_9H_5ClN.COOH$ , by phosphorus pentachloride, and by heating with hydriodic acid and phosphorus into the amorphous hydroquinoline,  $(C_9H_8N)_2$ . This last reaction shows that the hydroxyl-group is not in the benzene, but in the pyridine nucleus; and in the present communication this supposition is confirmed, and it is further shown that hydroxycinchonic acid is a carboxyl-derivative of carbostyryl.

The authors were unable to obtain a hydroxyquinoline by distilling hydroxycinchonic acid with bases; but on heating its silver salt,  $C_9H_5(OH).COOAg$ , in a current of carbonic anhydride, a sublimate was formed crystallising in needles, and having the characteristic properties of carbostyryl.

Chlorocinchonic acid, when heated with sodium alcoholate, yields *ethoxycinchonic acid*,  $C_9H_8N(OEt).COOH$ , which crystallises in hairy needles melting at  $145^\circ$ , soluble in hot water, alcohol, and dilute mineral

acids; its *silver* and *lead* salts are sparingly soluble precipitates, of which the former is an acid salt of composition

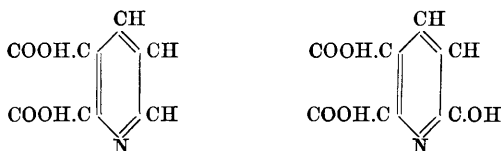


its platinumchloride,  $[\text{C}_9\text{H}_5\text{N}(\text{OEt}).\text{COOH}]_2.\text{H}_2\text{PtCl}_6$ , is crystalline.

When ethoxycinchonic acid is heated to a temperature slightly above its melting point, it is transformed into the isomeric ethyl salt of hydroxycinchonic acid,  $\text{C}_9\text{H}_5\text{N}(\text{OH}).\text{COOEt}$ , also obtained by the action of ethyl iodide on silver hydroxycinchonate. This salt crystallises in needles melting at  $206^\circ$ , and, unlike its isomeride, is insoluble in dilute acids or alkalis. The intermolecular change of the ethoxy-acid into the ethyl salt of the hydroxy-acid probably prevents the elimination of carbonic anhydride from the acid, when it is heated with lime. When the silver hydrogen salt is heated in a current of carbonic anhydride, ethylcarbostyryl and the ethyl salt of ethoxycinchonic acid are produced. The latter substance, which can also be prepared from ethyl iodide and the silver salt, crystallises in fine needles melting at  $86^\circ$ .

From these researches it follows that hydroxy- and ethoxy-cinchonic acids are derived from carbostyryl, and as cinchonic acid is converted into pyridine tricarboxylic acid by oxidation with potassium permanganate, the carboxyl-group is in the pyridene nucleus.

In cinchonic and hydroxycinchonic acids, the N-atom and the carbon to which the  $\text{COOH}$ -group is united, are probably in the para-position to one another. The authors have also succeeded in converting quino-  
linic, or pyridinecarboxylic acid, into hydroxyquinolinic acid by melting the former with potash. The relations of these acids is evident from the following formulæ:—



The latter forms colourless crystals melting at  $254^\circ$  of strongly marked acid properties; its aqueous solution gives a deep red coloration with ferric chloride, and voluminous precipitates with copper, lead, and silver salts. Its hydrogen barium salt crystallises in tufts of needles; its hydrogen silver salt, when heated in a current of carbonic anhydride yields a compound having all the characteristic properties of oxypyridine,  $\text{C}_8\text{H}_5\text{NO}$ .

V. H. V.

**Oxidation of Morphine.** By L. BARTH and H. WEIDEL (*Monatsh. Chem.*, 4, 706—703).—The action of most oxidising agents on morphine does not yield very definite results; potassium permanganate however in slightly alkaline solution acts on it somewhat more energetically, yielding as chief product a light-brownish uncrystallisable acid syrup, which forms amorphous salts, and when mixed with cupric acetate, remains clear at first, but becomes turbid on boiling, depositing a blue-green flocculent precipitate, which redissolves on cooling. This result is like that which is obtained by similar treat-

ment of cinchomeric and pyridine-tricarboxylic acids. Morphine subjected to dry distillation with lime yields a basic oil having a decided odour of pyridine. Arsenic acid acts but slowly on morphine even in sealed tubes, yielding a base which appears to contain one methyl-group less and one hydroxyl-group less than morphine; the action is however variable and so are the products. When morphine is heated with potassium hydroxide till the surface of the melt begins to glow, and the product, after cooling, is acidulated, brown-black non-nitrogenous flocks are deposited, and a solution is obtained from which ether extracts a considerable quantity of substance; and on expelling the ether, digesting the residue with water, precipitating the filtrate with lead acetate, decomposing the precipitate with hydrogen sulphide, evaporating, and repeatedly crystallising the residue, a product is obtained, consisting of protocathechuic acid. The filtrate freed from lead and evaporated yields more protocathechuic acid, together with another acid which crystallises in prisms, and gives no colour-reaction with iron salts.

When the melting with potash was conducted in a silver retort, and the vapours were received in dilute hydrochloric acid, methylamine was obtained, together with a small quantity of another base.

The absence of aromatic compounds amongst the products formed by oxidising morphine with permanganate, and the non-occurrence of derivatives of pyridine (or quinoline) in the oxidation of this alkaloid with caustic alkali, seem to show that the mode of combination of the aromatic and of the pyridine- (or quinoline-) groups in it, is different from that which exists in narcotine, which, it is well known, is easily resolved into its two principal constituents. H. W.

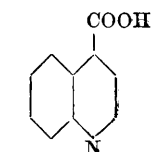
**Constitution of Quinine and Quinidine.** By Z. H. SKRAUP (*Monatsh. Chem.*, **4**, 695—699).—The author has already shown (*Abstr.*, 1882, 279) that these two alkaloids, when oxidised by chromic acid, yield carbonic anhydride and quininic acid,  $C_{11}H_9NO_3$ , which latter, when heated with hydrochloric acid, gives methyl chloride and xanthoquinic acid,  $C_{10}H_7NO_3$ , resolvable by heat into  $CO_2$  and a hydroxyquinoline,  $C_9H_7NO = C_9H_6(OH)NO_2$ ; further that quininic acid is converted by oxidation with permanganate into a pyridine-tricarboxylic acid,  $C_5H_2N(COOH)_3$ , identical with that which is obtained from cinchoninic acid: hence it is probable that quininic acid is a derivative of quinoline, and that its methyl-group is situated in the benzene-residue of the quinoline-molecule; hence also it may be inferred that the hydroxyquinoline obtained from xanthoquinic acid has its hydroxyl-group situated in the benzene residue. According to existing views there should be only four hydroxyquinolines thus constituted. Three are already known, and the main object of the present investigation is to ascertain whether the hydroxyquinoline obtained in the manner just mentioned is identical with either of these three, or consists of the hitherto unknown fourth modification.

Xanthoquinic acid is for the most part resolved at  $310^\circ$  into carbonic anhydride and a hydroxyquinoline, which when purified by conversion into platinochloride, &c., crystallises from absolute alcohol

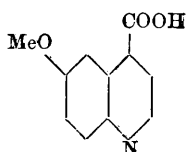
in slender white prisms, soluble in alcohol without coloration, the solution however acquiring, on addition of water, a faint yellow colour, which disappears on further addition of alcohol. This behaviour distinguishes the hydroxyquinoline in question from the *meta*-modification, the alcoholic solution of which exhibits a splendid green fluorescence. From the *ortho*-modification it is distinguished by giving, on addition of ferric chloride to its alcoholic solution, not a green, but a reddish coloration. With *para*-hydroxyquinoline on the other hand it agrees very nearly in its melting point ( $194^{\circ}$ ), and further in the yellow coloration of its alcoholic solution by ferric chloride; in giving with picric acid slender yellow prisms melting at  $235-235.5^{\circ}$ ; with cupric acetate, first a fine blue-green colour, then gradually violet prisms which dissolve in boiling alcohol with a fine leaf-green colour, and remain unaltered on evaporation.

This hydroxyquinoline dissolves readily when gently heated with four times its weight of strong nitric acid, and the solution, when quickly cooled and cautiously diluted with cold water, deposits orange-red crystals, easily soluble in hot water, the solution slowly mixed with potash-lye, depositing yellowish prisms, which, after recrystallisation from dilute alcohol, melt, like nitro-*p*-hydroxyquinoline, at  $140-141^{\circ}$ . The alcoholic solution, mixed with cupric acetate, first turns bright green, and then deposits a copper-brown precipitate, or if a trace of alkali be added, a green precipitate. The barium salt of the nitro-compound forms orange-red needles, slightly soluble in cold, much more freely in boiling water.

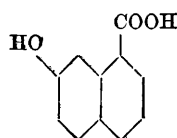
Cinchoninic, quininic, and xanthoquinic acids may be represented by the following constitutional formulæ:—



Cinchonic acid.



Quininic acid.



Xanthoquinic acid.

H. W.

**Cinchonamine.** By ARNAUD (*Compt. rend.*, **97**, 174—176. See also Abstr., 1882, p. 229).—Cinchonamine,  $C_{19}H_{24}N_2O$ , exists in *Remijia purdiana*, but is not contained in *R. pedunculata*, which contains quinine. To extract cinchonamine, the finely powdered bark is exhausted with very dilute sulphuric acid, the solution filtered, boiled, and precipitated with milk of lime. The precipitate is dried on porous tiles, and digested with boiling ether. The ethereal solution is decanted from undissolved resinous substances, &c., washed with dilute hydrochloric acid, which removes the cinchonamine, and the acid solution of cinchonamine hydrochloride is evaporated to crystallisation. The hydrochloride is dissolved in boiling dilute acid, filtered through animal charcoal, and recrystallised. The free base is obtained by adding ammonia to a solution of the hydrochloride, and crystallising the alkaloid from boiling ether. An alcoholic solution of the alkaloid is dextrogyrate, its rotatory power at  $97^{\circ}$  being

$[\alpha]_D = 122.2^\circ$ . According to Dr. Laborde, cinchonamine is highly poisonous, even in very small doses.

The salts of cinchonamine generally crystallise readily, and are but slightly soluble in water, especially in presence of free acid. They dissolve in hot alcohol, from which they crystallise on cooling. The *hydrochloride* crystallises from an acid solution in thin, brilliant, anhydrous, prismatic lamellæ, very slightly soluble in acidulated water. From a neutral aqueous solution, the salt crystallises in opaque flattened prisms containing 1 mol.  $H_2O$ . These crystals effloresce, and are much more soluble in water than the anhydrous salt. This property of the hydrochloride to crystallise in an anhydrous condition from acid solutions furnishes a method of separating cinchonamine from all the alkaloids with which it is associated in *R. purdiana*. The *hydrobromide* forms brilliant, slender, anhydrous needles, slightly soluble in cold water, much more soluble in hot water. The *hydriodide* crystallises in micaceous plates, almost insoluble in cold water. The *nitrate* is only slightly soluble in cold alcohol, but is much more soluble in hot alcohol, from which it crystallises in hard, thick, short prisms. This salt is slightly soluble in pure water, but is insoluble in acidulated water, and is precipitated on adding nitric acid to even a dilute aqueous solution of any cinchonamine salt. The precipitate is at first flocculent, but, on standing, it rapidly becomes crystalline, the crystals being small prisms, which polarise light. At  $15^\circ$ , 100 parts of alcohol of  $94^\circ$  dissolve 0.825 part of the salt; 100 parts of water at the same temperature dissolve 0.2 part of salt. The *sulphate* can be purified by crystallisation from alcohol. A solution of the salt in water containing 1 mol.  $H_2SO_4$  has a rotatory power at  $15^\circ$   $[\alpha]_D = +43.5$ ; at  $25^\circ$   $[\alpha]_D = +42.2$ . The *formate* crystallises with difficulty. The *acetate* is very soluble in water, from which it is deposited as a resinous mass on evaporation. By spontaneous evaporation of the aqueous solution the salt is obtained in deliquescent crystalline concretions. The *oxalate* does not crystallise from an aqueous solution, but is deposited in a resinous form. The *tartrate* forms a crystalline powder consisting of small hexagonal prisms which polarise light. 100 parts of water at  $15^\circ$  dissolve 1.150 parts of the salt. The *malate* forms brilliant nacreous plates, very slightly soluble in cold water, but somewhat soluble in boiling water. The crystals retain 1 mol.  $H_2O$  at  $120^\circ$ , but melt and become anhydrous at  $160^\circ$ . 100 parts of water at  $15^\circ$  dissolve 1 part of malate. The *citrate* is deposited from a boiling solution on cooling as a resinous mass, which gradually becomes crystalline, forming concretions composed of brilliant prisms which polarise light. 100 parts of water at  $16^\circ$  dissolve 1.950 parts of the citrate.

C. H. B.

**Conversion of Brucine into Strychnine.** By HANRIOT (*Compt. rend.*, 97, 267—268).—The author has repeated Sonnenschein's experiments (*Ber.*, 8, 212), and finds that strychnine is not produced by the action of nitric acid on pure brucine. Sonnenschein's experiments were probably made with impure brucine. Brucine has the power of completely masking the ordinary reaction for strychnine (with sulphuric acid and dichromate), even when the latter is present

to the extent of 50 per cent. It is evident therefore that the presence of strychnine in many samples of brucine may easily have been overlooked, and this will probably account for the confusion which exists as to the physiological action of brucine. Morphine, quinine, methyl alcohol, and many other substances also have the property of masking the strychnine reaction.

C. H. B.

**Products of the Bacterial Fermentation of Albuminoids.** By A. GAUTIER and A. ÉTARD (*Compt. rend.*, **97**, 263—267. See also Abstr., 1882, 1115; and 1883, 100 and 224.)—The authors have previously shown that the putrefaction of albuminoids results in the formation of leucines, glucoproteins, nitrogenous and non-nitrogenous acids, phenol, skatole, indole, tyrosine, trimethylamine, ammonia, and ptomaines. Whatever the variety of the ferment and the source of the putrefying flesh, the principal ptomaines formed are constant in properties and composition.

The liquid and solid putrid matter is distilled in a vacuum at a low temperature. The distillate (A) contains ammonium carbonate, phenol, skatole, trimethylamine, and volatile fatty acids; the residue is treated successively with ether and alcohol. The ethereal solution (B) contains ptomaines and a fatty acid, and holds in suspension very light, brilliant, white nacreous plates. The alcoholic solution (C) contains fatty acids and crystallisable nitrogenous compounds. The residue insoluble in ether and alcohol is boiled with very dilute hydrochloric acid out of contact with air, the solution evaporated and treated with alcohol (D).

The ethereal solution (B) when distilled leaves a brown oil, from which a large quantity of fatty acid crystallises out. The mother-liquor is acidified with sulphuric acid, saturated with potash, and agitated with ether, which dissolves the ptomaines. A solution of the ptomaines from beef treated in the cold with platinum tetrachloride, care being taken to avoid an excess, yields a precipitate of the composition  $(C_8H_3N)_2 \cdot H_2PtCl_6$ . It is the platinochloride of a hydrocollidine, identical with the base previously obtained from fish (*loc. cit.*). The mother-liquor from this platinochloride contains another platinochloride, which forms yellowish crystals of the composition C, 28.73; H, 5.8; N, 7.19; Pt, 27.93. It is partially decomposed at 100° with development of the hawthorn-like odour of its alkaloid.

The brilliant plates held in suspension by the ethereal solution consist of the calcium salt of amido-stearic acid,  $C_{18}H_{35}(NH_2)O_2$ . This is almost insoluble in all solvents, but is dissolved slightly by alcohol. When treated with hydrochloric acid, it yields amido-stearic acid, which is insoluble in water, only slightly soluble in cold alcohol, but readily in hot alcohol, from which it crystallises in aggregated needles on cooling. It melts at 63°, and when heated at about 140° it loses 1 mol. of water, and yields the anhydride,  $C_{18}H_{33}NO$ . The amido-stearic acid is obtained from beef: the nacreous plates obtained from putrid fish are soluble in alcohol and in potash, but are insoluble in water and acids. By treatment with inorganic acids they yield an acid of the composition,  $C_8H_{20}N_2O_3$ . When they are fused with



potassium hydroxide, ammonia is given off, and a mixture of alkaline caprylate, caproate, and acetate is formed.

The alcoholic solution (C) contains the greater part of the leucines and leucoproteins. After evaporation, the residue is treated with inorganic acids, the aqueous liquid separated from the liberated fatty acids, concentrated by evaporation, and treated with alcohol, which dissolves out leucines and leuceines, particularly those containing  $C_5$  and  $C_6$ . The principal compound thus obtained from putrid fish forms white rhomboidal lamellæ, somewhat soluble in water, and somewhat easily sublimed; it has the composition  $C_{11}H_{26}N_2O_6$ , and appears to be the hydroxide of the glucoprotein,  $C_{11}H_{22}N_2O_4$ , obtained by Schützenberger from the products of the decomposition of albuminoids by baryta. It has the general properties of amido-acids, and dissolves in dilute alkalis; when fused with potassium hydroxide, it yields hydrogen, ammonia, and potassium carbonate, butyrate, and valerate, a portion splitting up at the same time into the corresponding leucines and leuceines. When distilled at about  $280^\circ$ , it yields an amylamine boiling at  $92-93^\circ$ , which is probably formed together with amido-valeric acid in accordance with the equation  $C_{11}H_{26}N_2O_6 = C_5H_{13}N + C_5H_9NO_2 + CO_2 + 2H_2O$ .  
C. H. B.

**Albumin, Nuclein, and Plastin.** By E. ZACHARIAS (*Bied. Centr.*, 1883, 405—407).—The principal portions of the nitrogenous substances of plant cells, insoluble in alcohol, consist of albumin, nuclein, and plastin, the two latter are attacked but slightly, or not at all, by the gastric juices; on the contrary, they readily dissolve albumin. Plastin is insoluble in very dilute solutions of alkalis, nuclein is easily soluble in these menstrua; plastin and nuclein are the soluble and insoluble nucleins of other authors. The supposition of Schimpers that the substance from which starch is produced is similar to albumin, at least to a great degree, the author believes he has confirmed by researches on the leaves of *Tradescantia virginica* and orchis.

Albumin diminishes and plastin increases in the protoplasm of the cells examined; according to Hartig's reaction, sections soaked in a dilute solution of potassium ferrocyanide, and then transferred to a very dilute solution of ferric chloride, show the nucleus deep blue, whilst in the ducts no trace of a blue colour is visible. When portions of the epidermis of the leaves of those plants are so treated, the starch material becomes intensely blue, the cell protoplasm remains colourless, or is coloured only in points. The nuclei show a blue coloration, as also the nucleoli; the plastin is colourless or very slightly coloured.

The author does not think that the chemical constitution of the nuclei and nucleoli can be ascertained from these reactions, but they are aids to that knowledge.  
J. F.

## Physiological Chemistry.

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**Influence of Respiration on Elimination.** By F. PENZOLDT and R. FLEISCHER (*Bied. Centr.*, 1883, 285).—Want of oxygen sufficient to induce the dyspnoëic condition, causes an increased excretion of urine and urea, as also of phosphoric acid; the after-action is lowering of phosphoric acid, but raising of urea, the absolute result being no change in the total excretion of acid and urea, and no separation of sugar or albumin. If, however, the animal is fasting, then whilst there is a want of oxygen, there is a slight increase in urine, a considerable rise in urea and phosphoric acid; during the after-action urea still increases, but phosphoric acid decreases, so that there is an absolute increase in the excretion of urea, but no phosphoric acid, albumin, sugar, nor allantoin. When no dyspnoëa accompanied the want of oxygen, then a well-nourished dog excreted more urine and phosphoric acid, but less urea, whilst during the after-action there was an increase in water, urea, phosphoric and sulphuric acids. On the whole, an absolute increase of these four compounds with traces of albumin; the case was similar when a fasting dog was experimented on, save that sodium chloride behaved as urea.

The diminished supply of oxygen when accompanied by dyspnoëic action affects birds, and causes them to excrete an excess of uric acid. Apnoëa causes a rise of urea, a fall of phosphoric acid, and afterwards a considerable increase of both. Increased elimination of water is accompanied by a lowered excretion of urea. Increased muscular action induces great increase of urea, at first a large decrease, later on an increase, and on the whole a slight absolute increase of phosphoric acid. Reduction of the temperature of the body is followed by increase of urea.

E. W. P.

**Exhalation of Carbonic Acid by Frogs.** By H. AUBERT (*Bied. Centr.*, 1883, 427).—The author finds that the process of exhalation is as active in an atmosphere which is deprived of oxygen as in one which contains it. The same observation has been made by Pflüger, and can only be explained on the supposition that the process depends on the decomposition of organic compounds independent of the presence of atmospheric oxygen.

J. F.

**Alteration of Cane-sugar in the Human Stomach.** By W. LEUBE (*Bied. Centr.*, 1883, 427).—100 c.c. of a 10–15 per cent. cane-sugar solution were introduced into an empty stomach seven hours after a previous meal, or in the morning before the subject had eaten, the stomach having been previously rinsed and the rinsings tested with Trommer's test to negative reaction. Half an hour after introducing the sugar, there was no reaction, or very trifling, whereas in a known unhealthy stomach the reaction was considerable. The explanation appears to be that in the healthy stomach the inverted sugar is absorbed, which is not the case in the unhealthy one. The gastric

juices of both healthy and sick persons cause the inversion of cane-sugar equally outside the body, but if a solution is introduced in equal parts into the stomachs of living subjects and withdrawn half an hour afterwards, the difference in the reducing power is most marked, the healthy stomach showing no reaction, whilst the unhealthy does very strongly. J. F.

**Comparative Value of Artificial and Natural Butter as Articles of Food.** By A. MAYER (*Landw. Versuchs.-Stat.*, 29, 215—232).—In estimating the value of any article of food, the points to be dwelt on are chiefly its nutritive qualities, taste, and action on the system, whether injurious or otherwise. In the case of butters of various origin, the last two points are easily settled, as a positively injurious influence has never been seriously ascribed to artificial butter. The nutritive qualities of butter were therefore the subject of this investigation.

Experiments were made with a man and a boy, who received a certain quantity of food per diem, as to whether artificial or natural butter was the more easily absorbed by the system. The first three days they were fed with various mixtures of bread, milk, eggs, and vegetables, together with natural butter; then followed two days' rest with ordinary diet, and afterwards three days with precisely the same diet as before, with the exception that artificial was substituted for natural butter. On each successive day of the experiment the solid evacuations were collected and analysed, commencing 24 hours after the beginning of the experiment. The amount of fat in these was estimated, and hence the quantity of fat absorbed into the system was found. This quantity is given in percentage of the whole amount in the food in the table below:—

<i>Man.</i>			
Day of experiment.			
	1.	2.	3.
Natural butter .....	97·0	99·4	98·7
Artificial „ .....	94·6	97·9	96·7
<i>Boy.</i>			
Natural butter .....	97·8	94·8	98·7
Artificial „ .....	95·3	94·6	97·6

On the average, therefore, about 1·6 per cent. less of the artificial butter was absorbed than of the natural. As this quantity is, however, very small in comparison to the total amount absorbed, the difference in value of the two substances as articles of food can be set down as only trifling, and except in cases of illness may be overlooked with safety. J. K. C.

**Digestive Fluid and Digestive Power of the Horse.** By ELLENBERGER and HOFMEISTER (*Bied. Centr.*, 1883, 386—389).—It being difficult to obtain the natural digestive fluid of the horse, an artificial

one was prepared by cutting up the coating of the stomach containing the ducts into very small bits; it was then washed and neutralised, either at once or after treatment with alcohol, dried, and left from 24 hours to eight days in contact with an extracting fluid, which treatment dissolves out all the ferments and acids. The fluids used were:—1. Water; 2, glycerol; 3, 0·2 to 0·5 per cent. HCl; 4, 0·2 to 0·5 per cent. lactic acid; 5, 0·2 to 0·5 HCl in glycerol; 6, same proportion lactic acid in glycerol.

The extract obtained from the part near the intestine contained more mucin, acids, and ferments, and dissolved albumin more easily than the extract from the region of the pylorus.

The extract from the whole stomach contains both hydrochloric and lactic acids, but not more than 0·04 per cent. apparently. It also contains a very active ferment, which alters albuminous substances to peptones, and so changes gelatin that it becomes easily diffusible and loses its properties. The ferment is sparingly soluble in water, glycerol, hydrochloric acid, or in alkaline solutions, and it is precipitated by alcohol, lead acetate, carbonate of magnesia, &c. It is only active in presence of acids, and is destroyed by putrefaction and alcoholic yeasts. Lactic ferments do not influence its activity when the lactic acid is not too highly concentrated. Its activity is greatest in presence of 0·15 to 0·5 per cent. hydrochloric acid; too much or too little acid impedes the action of the pepsin, much lactic acid in the stomach disturbs the digestion through irritation of the coating of the stomach.

Pepsin must be present in certain quantity in the digestive fluid; its activity increases according to its quantity up to a certain point, when further quantity is injurious. It works only in presence of water, and best at a temperature of 37° to 55°; raising and lowering the temperature disturbs the operation; at 60° it becomes quite inert. Pure gastric juice contains rennet, lactic acid, fat and starch ferment, the two latter in unimportant quantity.

The gastric juice of the horse does not dissolve cellulose, and with difficulty the substance of bone or horn, but acts readily on muscle, sinew, fat, and flesh. Pepsin extract may be preserved for a long time in weak carbolic or salicylic acid solution, and even in pure glycerol without losing its properties. J. F.

**Milk Secretion.** By SCHMIDT (*Bied. Centr.*, 1883, 382—386).—The author, after reviewing much of the previous literature of the subject, reports the result of his own investigations on the activity of the milk glands of the cow: the experimental animal was of Dutch breed, middle aged, yielding 12 litres of milk daily. The experiments were conducted thus: 500 c.c. were taken from the two hinder spins of the udder at the commencement of the morning milking, and the same quantity from the same spins at the conclusion of the milking; both were carefully analysed according to the usual methods. Only the results of the first day's analysis are given, the others differing slightly, if at all, and not affecting the author's conclusions. 100 grams of the milk contained—

	First milk.	Last milk.
Total solids . . . . .	9.20 grams.	13.64 grams.
Casein . . . . .	2.24 „	2.11 „
Albumin . . . . .	0.31 „	0.29 „
Peptone . . . . .	0.10 „	0.12 „
Fat . . . . .	0.76 „	5.60 „
Sugar . . . . .	5.08 „	4.92 „
Ash . . . . .	0.69 „	0.66 „

It will be seen that the difference between the total solids consists almost entirely in the fat, which is almost absent from the first milk; this is explained by the theory that the fat corpuscles of the milk adhere to the walls of the ducts, and besides that in the udder itself a certain separation takes place. The author had an opportunity of examining the udder of a cow killed immediately after milking, and found that the ducts did actually contain a notable residue of rich milk.

The fat excepted, the great body of milk secreted by a cow appears to have a tolerably uniform composition, and the separation of the fat in the udder to be a mechanical operation, and that the whole of the fat is rarely obtained in the milking. J. F.

**Percentage of Fat in Milk of Cows of Different Breeds.** (*Bied. Centr.*, 1883, 285.)—Pure Simmenthal gave 13 per cent. cream, after 12 hours' standing; Dutch, 7 per cent. cream, after 24 hours, 8 per cent.; cross between Simmenthal and Graubünden, 12 per cent., after 24 hours, 12.5 per cent.; cross of Dutch and Simmenthal, 9 to 9.5 per cent.; pure Graubünden, 13 per cent.; cross between Dutch and Graubünden, 10 per cent. E. W. P.

**Excretory Product from the Liver of the Cuttle Fish.** By A. B. GRIFFITHS (*Chem. News*, 48, 37).—The author observed some peculiar roundish masses of a dark-coloured substance in the anterior portion of the liver of the cuttle fish; some of these were collected and examined. When ignited, they charred, and left an ash, which contained copper. The following are the results of observations made under the microscope: the masses were stained brown by a solution of iodine in potassium iodide; potash dissolved them; a red colour was produced with Millon's reagent; and nitric acid produced a yellow coloration, which was turned red by potash. On boiling them with hydrochloric acid, a blue colour is formed, which changes to violet, and finally becomes brown. On heating them with solid potash, ammonia is evolved. By boiling a solution of the substance in potash with lead hydroxide, lead sulphide is produced. From these results the author infers that these masses are albuminoid in character, and assuming them to be deposited from the secretion, it is evident that the secretion must contain albumin; and as the pancreatic fluid in higher animals is one of the few secretions which contain soluble albumin, the author is of opinion that this investigation supplies further support to the supposition that the liver of the cephalopod is not a true liver, but is pancreatic in function. The copper is derived

from the blood. The dark colour of the masses was a very thin superficial covering.  
D. A. L.

**Behaviour of Blood with Ozone.** By BINY (*Bied. Centr.*, 1883, 283).—The red corpuscles in blood are unaffected by remaining for an hour in contact with ozone, unless the quantity of blood is small, or the duration of contact long; then a gradual change of colour and shape occurs. Ozonised air passed through blood is not completely altered.  
E. W. P.

**Cattle Disease occasioned by Town Sewage.** (*Bied. Centr.*, 1883, 285).—The death of many cows was occasioned by fungoid growths in the grass of meadows irrigated with sewage.  
E. W. P.

**Observations on Different Diseases of Animals.** By ROLOFF and others (*Bied. Centr.*, 1883, 389—393).—Experiments were made at the Veterinary School, Berlin, by Roloﬀ, on the protective inoculation of cattle against lung disease. Two cows, two heifers, and two calves were inoculated with the preparation and placed in infected stables; none of them took the disease, but neither did a non-inoculated animal placed in the same stable: the experiment was therefore abortive. Opinions of other observers are cited on the question of protective inoculation against this particular disease. Pasteur finds that the specific poison cannot be cultivated in chicken or veal broth; that it preserves its vitality when kept at a high temperature in a dry room, and does not produce micrococci, but that, when kept without such precaution, it does produce them and loses its vitality.

If the poison is fouled by the addition of a few cow hairs before use, it is harmless; the portion kept at ordinary temperatures reproduces itself in the inoculated animal, and lymph taken from that animal communicates it to others. After six to eight weeks from taking the poison from an infected animal, it loses its vitality: a calf into whose jugular vein such old poison was injected, withstood it. The discovery of the bacillus of glanders by Löﬂer and Schütz is next noticed; the rods were isolated from sections of a diseased organ, and cultivated in the blood of horses and sheep. It was tried on rabbits, mice, and guinea-pigs with success, but white mice did not take the infection. The material used for inoculation was cultivated for eight to ten weeks, and then used on two horses, one two years old, the other 20 years. Both died with all the symptoms of virulent glanders in about 12 days.

Pasteur and Thullier report the discovery of the microbe which causes swine fever, a disease by which, in the year 1882, farmers of the Rhone Valley lost 20,000 animals. The microbe is very minute and liable to be overlooked even when the greatest care is used in its observation; it resembles that of chicken cholera, and is of the form of the figure 8. Inoculation by a very small quantity communicates the disease; poultry are not affected, but rabbits die. The infection has been cultivated and weakened, so as by its inoculation to protect swine

from fatal effects. Pasteur hopes soon to prevent the heavy losses sustained from this cause.

The remainder of the paper relates to osteoporosis, or bone weakening in animals, horses and swine particularly. Pütz attributes it to continued feeding on bran and other fodder poor in lime.

J. F.

**Cattle Plague and Protective Inoculation.** By KOCH and others (*Bied. Centr.*, 1883, 394—398).—Koch considers that Pasteur's mode of procedure is not quite correct, but liable to yield uncertain results. He thinks that the bacilli of the disease are propagated independently of animals; that they exist on dead vegetable substances, and probably on low marshy soils, on the surface of the earth; and he says that animals have been known to take the disease in such places where no diseased carcasses had been buried. He denies the agency of earthworms in bringing the disease germs to the surface, for the plague appears in countries where the low temperature of the soil does not permit the existence of earthworms. He also denies Pasteur's assertion that the eating of the prickly fodder wounds the mouth and facilitates the taking of the disease.

The weakening of the poison, and the protection given by inoculation, has been successful only with horned cattle and sheep, and Koch doubts if the lymph is as successful, even with those animals, as Pasteur believes. The most carefully conducted experiments made with it in Germany show a loss of 10 to 15 per cent. of the inoculated animals, and there is danger to men by its employment. Koch does not undervalue the researches of Pasteur, but wishes to point out deficiencies in this particular case, which any day may be supplied. Instances are given of the deaths of sheep from plague, which had been duly inoculated. Dr. Azary gives results of numerous inoculations by Pasteur's fluid in the neighbourhood of Buda Pest, chiefly with sheep, also with horned cattle and horses; some losses took place, but on the whole the operations were successful. Arloing and others have experimented on the duration of the protective influence, and found it lasted at least 16 months; and that calves born of inoculated cows were not liable to disease for some time after their birth.

J. F.

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### Chemistry of Vegetable Physiology and Agriculture.

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**Occurrence of the Higher Fatty Acids in the Free State in Vegetable Fats.** By E. SCHMIDT and H. ROEMER (*Arch. Pharm.* [3], 21, 34—38).

*The Fat of Cocculus indicus.*—The fat which is contained in the seeds of this plant was dissolved in alcohol and precipitated with an alcoholic solution of barium acetate, by which means the free fatty acids were separated from the glycerides with which they are asso-



ciated in the original fat. After boiling for some time, the barium precipitate was filtered off, and when dry boiled with light petroleum. The nearly pure barium salt thus obtained was decomposed with hydrochloric acid. In this way 39 per cent. of free fatty acid was yielded by the original fat. By this means and by repeated crystallisation of the original fat from alcohol, as well as by distillation under diminished pressure, and also by partial precipitation with barium acetate, an acid was obtained which was recognised by analysis and physical properties as stearic acid. The substance obtained from *Cocculus indicus*, known as *menispermin*, was found by the authors to consist of stearic acid.

*The Fat of Myristica moschata*.—This fat, commonly known as nutmeg butter, or oil of mace, contains from 3—4 per cent. of free fatty acid, which was separated by fractional distillation under diminished pressure. At  $248^{\circ}$  the distillate, after recrystallisation from alcohol, yielded an acid, the formula of which was  $C_{14}H_{26}O_2$ , agreeing in its properties with myristic acid. The distillate, which came over at a higher temperature, was partially precipitated with barium acetate, and the acid which was recrystallised from alcohol, and analysed, gave numbers agreeing with the formula  $C_{18}H_{36}O_2$ , and was identical in physical properties with stearic acid.

*The Fat of Laurus nobilis*.—This fat, when distilled under diminished pressure, yielded a distillate, by the fractional precipitation of which an acid was obtained, which appeared to be palmitic acid.

W. R. D.

**Chemistry of the Nucleus.** By A. KOSSEL (*Bied. Centr.*, 1883, 401—404).—The regular relations between phosphoric acid and nitrogenous matters, which have been noticed both in vegetable and animal cells, have given rise to the idea of a compound of albumin and phosphates or phosphoric acid. In all the discussions on the subject, it seems to have been overlooked that lecithin and nucleïn are organic phosphorus-compounds, which are sufficient to explain these appearances. Among the products of their decomposition, the author found a body which had almost the identical percentage composition of albumin. The usual mode of estimating nucleïn is by its resistance to the action of pepsin, but the author considers this liable to great error, and prefers a plan of his own. He found this phosphoric compound in the organs examined—in the spleen, liver, pancreas, kidneys, testicles, brain, embryonic and grown muscles of animals, pus, and in human dropsical and healthy blood. According to experiments made with hens, doves, and yeast, the author regards nucleïn as a reserve material on which the organs subsist, or from which they draw supplies, to be incorrect; he finds hypoxanthine and xanthine to be characteristic decomposition products of nucleïn, and guanine accompanies them in many organs; this by oxidation yields guanidine and urea. The fact that a substance exists in most animal organs, which furnishes urea by simple oxidation, he thinks important from a physiological point of view.

J. F.

**Flowers of Rosa Centifolia.** By NIEDERSTADT (*Landw. Versuchs.-Stat.*, 29, 251—252).—Red roses were found to contain 86 per cent.

of water, 3·64 per cent. nitrogen, and 3·5 per cent. ash; in white roses were found 91·7 per cent. water, 3·16 per cent. nitrogen, and 3·9 per cent. ash. The composition of the ash of each is given below:—

	Red roses.	White roses.
Potash .....	43·81	42·05
Soda .....	1·12	1·53
Lime .....	6·02	8·05
Magnesia .....	6·27	6·41
Ferric oxide and Alumina....	1·05	1·97
Phosphoric acid .....	16·47	11·32
Sulphuric acid .....	7·81	5·07
Silica ....	1·49	2·40
Chlorine .....	0·69	4·28
Carbonic acid .....	15·38	17·83

J. K. C.

**Ash of Leaves of Plants Grown in the Earth under Water-culture.** By C. COUNCLER (*Landw. Versuchs.-Stat.*, **29**, 241—245).—Several samples of *Acer negundo* were grown in a glass house, Nobbe's method of water-culture being used. The leaves were collected after falling, dried and analysed. At the same time leaves were carefully gathered from young trees of the same kind in a neighbouring wood, to compare with those obtained by water-culture. The percentage of pure ash in the leaves varied considerably, nearly twice as much being obtained from those grown by water-culture. In 100 parts ash were found—

	Water-culture.	Soil.
Potash .....	45·52	33·91
Soda .....	0·58	0·66
Lime .....	14·92	27·23
Magnesia .....	3·55	4·71
Ferric oxide .....	0·91	0·92
Alumina .....	—	4·00
Phosphoric acid .....	12·21	3·43
Sulphuric acid .....	18·30	7·29
Silica .....	4·00	17·85

The leaves of the soil plants contained, therefore, nearly twice as much lime, and more than four times as much silica as those of the plants grown by water-culture, whilst the latter contain much larger quantities of potash, phosphoric and sulphuric acids. These differences are no doubt in great part due to the soil in which the plants were grown; it is very rich in potash, but comparatively poor in phosphates.

J. K. C.

**Examination of an Apple-must and of the Cider obtained therefrom.** By R. KAYSER (*Dingl. polyt. J.*, **248**, 347).—Borsdorf apples were cut into small pieces and pressed. The resulting must was then tested before and after fermentation. 100 c.c. gave—

	Must (filtered).	Cider.
Alcohol .....	—	5·80 c.c.
Extract .....	16·25 g.	2·36 g.
Mineral matter (ash) ..	0·35	0·31
Malic acid. ....	0·33	0·31
Acetic acid .....	—	0·080
Sugar .....	12·50	0·750
Pectins .....	0·62	traces
Potash .....	0·106	0·105
Lime .....	0·025	0·024
Magnesia .....	0·018	0·018
Phosphoric acid .....	0·024	0·022
Sulphuric acid.....	0·009	0·008
Glycerol .....	—	0·680

Tartaric and citric acids were not present: hence cider can be distinguished from wine by the entire absence of tartaric acid, and by the larger amount of lime which it contains. By a judicious addition of tartaric acid or of wine containing much acid, a product can be obtained, which it would be difficult to distinguish from real wine.

D. B.

**Analysis of "Tobacco Stems" from Virginia.** By C. G. MEMMINGER (*Chem. News*, 48, 110).—"Tobacco stems" consist of the midribs of tobacco leaves from which the membranous portions have been stripped. The analytical results are as follow:—

<i>In original substance.</i>	<i>In organic matter.</i>
Moisture at 100°..... 17·52	Nicotine .....
Total ash, excluding CO <sub>2</sub> 16·47	N as nicotine .....
CO <sub>2</sub> determined .....	N as nitrate .....
(CO <sub>2</sub> calculated = 6·73)	N as albuminoid (by diff.)
Organic matter (by diff.) 59·41	<hr/>
<hr/>	Total N .....
100·00	2·18

<i>In ash.</i>					
K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .
42·95	6·53	24·56	6·20	0·04	0·84 per cent.
Mn <sub>3</sub> O <sub>4</sub> .	SiO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	Cl.	
0·09	6·18	4·80	3·10	6·04 per cent.	

D. A. L.

**Phylloxera.** By HENNEGUY and others (*Bied. Centr.*, 1883, 272—274).—Henneguy found the galls on many American pines, especially *Pinus riparia*, and but seldom on native vines; in large galls, several young insects have been found besides the egg producers, and Henneguy found thiocarbonate a good specific against the attacks. E. Cheysson approves of carbou bisulphide. A. Guillaumont states that a mixture of 10 parts wood-ashes, 10 ferrous sulphate, and 2 coal-tar, is a good specific for destroying the phylloxera.

E. W. P.  
h 2

**Valuation of Fodder.** By A. EMMERLING (*Bied. Centr.*, 1883, 252—255).—The relative value of albuminoids to fat and to carbohydrates is taken as 5 : 5 : 1. Multiplying each of these factors by the corresponding figures representing the digestible material in the food, we obtain a figure representing the sum of nutrient units. As a standard, rye is employed thus: Albuminoids, 9·9 per cent.; fat, 1·6; carbohydrates, 65·4, which figures, when treated as above,  $9·9 \times 5 + 1·6 \times 5 + 65·4 \times 1$ , produce 122·9 n. u.; and, taking 8 marks per centner as the market value of rye, 1 n. u. costs 6·5 pfennigs. Employing this method the feeding value of any material may be calculated; for example, in earth-nut cake we have albuminoids 45, fat 7, carbohydrates 25, of which the digestible coefficients are 90·9, 85·7, and 98·1 respectively, giving digestible matter present to the extent of 40·9, 6·0, and 24·5. Then  $40·9 \times 5 + 6 \times 5 + 24·5 = 259$  n. u.; and having laid down a table of the value of nutrient units for grain and other foods, which units vary according as the price of rye rises or falls, the author shows that when rye is at 8 marks the value of these 259 n. u. of earth-nut cake is 10·10 marks; but this cake only costs 9 marks, consequently there is a gain in using it. A similar method is employed to calculate the value of foods for manures, employing in this case the factors 0·5 for N, 0·2 for  $P_2O_5$ , and 0·1 for  $K_2O$ : by this he shows the manurial value of a centner of earth-nut cake to be 4·04 marks, and this, with the exception of cotton-cake, is the most valuable of all foods.  
E. W. P.

**Examination of Clover at different Stages of Growth.** By J. P. KALLEN and A. STUTZER (*Bied. Centr.*, 1883, 410—411).—Part of a series of experiments made in order to ascertain the period at which grasses contain most nutritive matter, with a view to harvesting them at such times. A field sown with red clover and different grasses, chiefly English rye-grass, was the subject of experiment: a square meter was cut on 17th, 24th, 31st May, and 20th June, and examined. The results are given in a table, and the recommendation is made to cut at the end of May or early in June.  
J. F.

**New Fodder Plant.** By F. T. (*Bied. Centr.*, 1883, 287).—*Javatera arborea* yields an oily seed, which after expression of the oil forms a good cake for cattle, and good fibre for paper making, rope, and cord. The plant is biennial, and crops well.  
E. W. P.

**Feeding Horses with Earth-nut Meal.** By C. FREYTAG and BECKE (*Bied. Centr.*, 1883, 284).—Earth-nut meal may well replace two-thirds of the oats generally given to horses.  
E. W. P.

**Storage of Acorns.** By LODEMAN (*Bied. Centr.*, 1883, 286).—Collect as late as possible, pile in heaps 30 c.m. high, cover with leaves and pine twigs; in the spring remove the covering to retard germination.  
E. W. P.

**Undecorticated Cotton-seed Meal.** By DIETRICH (*Bied. Centr.*, 1883, 428).—A considerable quantity of this article has lately been

sent from England to Germany; it is less valuable than the meal made from the decorticated seed, and is of a dark colour. Two samples had the following composition:—

	1.	2.
Proteid matter .....	23·56	23·06
Fat .....	6·26	7·01
Non-nitrogenous extract....	24·94	27·12
Cellulose .....	25·73	25·53
Mineral matters .....	8·15	6·59
Water.....	11·36	10·69

J. F.

**Cultivation and Preservation of Potatoes.** By MÄRCKER and others (*Bied. Centr.*, 1883, 268—270).—Stappaerts removes all eyes save three, and by setting only large sets obtains a higher yield, which ripens early. Märcker has preserved potatoes in a silo, when the nutrient ratio is increased by fermentation from 1:10 to 1:17·6; much of the albuminoid and amido-constituents are lost. L. Nagy enumerates and classifies the sorts of potatoes; he divides them into 12 principal classes, with 30 sub-classes.

E. W. P.

**Experiments on Potatoes with different Manures.** By E. W. PREVOST and R. SWANWICK (*Trans. Highl. and Agr. Soc.*, Scotland, 1882, 283—299).—In these experiments the actions of “bone,” “mineral,” superphosphates, and insoluble phosphates (85·5 per cent.  $\text{Ca}_3\text{PO}_4$ ) were employed, likewise an addition of ammonium sulphate, kainite, and potashes to the phosphates was made, with the results as hereinafter stated. The potato employed was the Champion, and the soil divided into plots of  $\frac{1}{11\frac{1}{2}}$  acre, contained 62 per cent. sand,  $\text{Al}_2\text{O}_3$  8·114,  $\text{K}_2\text{O}$  0·764, N 0·39,  $\text{NH}_3$  and  $\text{P}_2\text{O}_5$  0·284; all the plots were in triplicate. The “unaided” phosphates produced nearly equal crops, but the addition of 2 cwt.  $\text{Am}_2\text{SO}_4$  caused the bone super to produce the highest yield obtained, viz., 12 tons 12 cwt., whilst the blank plots only yielded 7 tons 4 cwt., and insoluble phosphate with ammonia 9 tons 15 cwt. The addition of potash to the mixture of “super” and ammonia rather lowered the yield, and but little difference was noticed when kainite or potashes were employed. This however was not the case with the insoluble phosphate, for then potashes increased the yield by a tenth. Farmyard manure gave only a moderate yield. In the second portion of this paper are the analyses of the potatoes as produced under the above conditions: the highest percentage of starch was found in potatoes grown with bone superphosphate, and taking the average of all the plots, it appears that the further addition of ammonia or kainite lowers the percentage, which is however raised again by potashes; but there is a great difference between the percentage of starch from the bone super plot and from the “insoluble” plot, the former being 25·6, the latter only 21·96. The expenses of the whole experiments are detailed, as also the value of the various crops, and we find that whether we judge the value of the manure by the total crop it yields or by the production of starch, the mixture of bone superphosphate

with ammonia was the most satisfactory. The effect on the amount of nitrogen present is also detailed, not merely as total nitrogen, but as nitrogen in amides and in albumin; ammonia increases the albuminoid nitrogen, but the increase is somewhat counteracted by potash, the unmanured plot containing least. The amides were likewise increased by ammonia (av. = 0.1399 N), but again kainite exercised a lowering action: an extraneous experiment is here referred to, which points to the conclusion that the amide nitrogen is much decreased as the ratio of potash to "super" increases. Phosphates and ammonia produce the highest ash (1.31), whilst in the superphosphate plots the percentage is reduced almost to that found in the blank plot (0.995); this is in accordance with the results found by Fleischer (*Bied. Centr.*, 1880), what has been said for ash holds good for fibre. Attempts were made to estimate the percentage of starch by the method recommended by Heidepriem (*Landw. Versuchs.-Stat.*, 20), but they were fruitless, as the results were very far from the truth, and therefore untrustworthy.

E. W. P.

**Influence of Manuring on the Composition of Potatoes.** By M. MÄRCKER (*Bied. Centr.*, 1883, 365—366).—Four plots of ground, each half a morgen loamy marl, on which barley and clover had been previously grown, were planted with "alcohol" potatoes; one plot was left unmanured, the other three each received 20 lbs. of soluble phosphoric acid, and different quantities of Chili saltpetre, the first 100 lbs., the second 200 lbs., the third 300 lbs. The yield per morgen was—

	Unmanured plot.	100 lbs.	200 lbs.	300 lbs.
Centner . . . . .	112.0	28.0	124.5	139.0

the use of the saltpetre had therefore increased the gross weight of the crop, but the percentage of dry matter and starch did not correspond, being—

Dry matter . . . . .	24.80	23.50	22.50	20.90
Starch per cent. . .	77.51	77.07	73.95	63.64

the use of large quantities of saltpetre having reduced the net quantity of starch, the actual amounts obtained being—

Plot 1.	Plot 2.	Plot 3.	Plot 4.	
21.58	23.18	20.74	18.43	centner.

J. F.

**Artificial Manures in Potato-growing.** By S. GURADZE (*Bied. Centr.*, 1883, 377—379).—The author reports five experiments as to the effect of different chemical manures on the growth of potatoes, combined in different proportions; they consisted of a newly introduced potash magnesia (containing 50 per cent. potassium sulphate, and 34 per cent. magnesium sulphate) superphosphate, and Chili saltpetre. All the experimental plots but two received a considerable quantity of stable manure, in addition to the artificial. The crops were in all cases exceptionally good, and the plants healthy; the pro-

portion of starch in the tubers good, and the value of the increased production repaying the extra cost of the manures employed. The author strongly recommends the use of artificial fertilisers in the growing of potatoes. J. F.

**Manuring Experiments with Rye and Wheat.** By M. MÄRCKER (*Bied. Centr.*, 1883, 373—377).—The first experiments noted were made with rye, on a good sandy soil, in order to observe the effects of phosphoric acid in bone-meal and in purely mineral phosphates, blood-meal being added to the latter equal to the nitrogen in the bone-meal. The quantity of phosphoric acid used was 10 kilos. per morgen, applied in autumn. The experiments were carried out by five farmers, independently of each other; the results were slightly in favour of the mineral phosphate with blood-meal. Steamed bone-meal produced good crops, the net result of the experiment being that a nitrogenous manure mixed with phosphate is most useful. Similar experiments were made on light and poor sandy soils with a different result, the steamed and fermented bone-meal giving the best crops, the other manures not repaying the extra cost. Certain plots of wheat were manured with Chili saltpetre, and others with ammonium sulphate, with a view of testing their manurial value. The manures were applied at different periods, the Chili saltpetre was found greatly superior, and the superiority was most marked when it was applied in May. The yield of both grain and straw was considerably larger than from all the other plots. J. F.

**Manuring Vines.** By A. STUTZER (*Bied. Centr.*, 1883, 381—382).—Vineyards in the Ahrthal have generally been manured with stable manure. The author found that a compost containing 7 per cent. soluble phosphoric acid, 6 per cent. potash, and  $2\frac{1}{2}$  to 3 per cent. nitrogen, applied in 100 gram doses to each vine, produced an average increase of 20 per cent. grapes more than the stable manured plants, and that the must was also richer in sugar. The cost of the manure and labour was not greater than that of the stable manure employed; the wood of the vines was stronger and healthier. J. F.

**Manuring Beet.** By HOLDEFLEISS (*Bied. Centr.*, 1883, 380—381).—The author recommends a moderate use of stable manure supplemented by Chili saltpetre as being most suitable for the full production of sugar in the beet. Manures which are too rich in nitrogen, such as sheep dung, or even too much Chili saltpetre, are decidedly injurious. In the absence of stable manure, a mixture of superphosphate with the saltpetre should be employed. J. F.

**Influence of Soil, Size of Seed, Period of Sowing, &c., on the Quality and Yield of Sugar-Beet.** By G. MAREK (*Bied. Centr.*, 1883, 263—268).—The weakest growth was in sandy soil, better on sandy loam, strong on clay and humous sand, and luxuriant on moorland; as regards the leaf growth, this was most abundant on the humous soil, and this class of land also is most suitable for a heavy crop; but the opposite is the case as regards sp. gr. of juice, for there

the clay lands are most advisable, and this is true for the percentage of sugar: the size of seed is not of much importance. The highest yield is obtained when the crop is put in between the middle of April and end of May. It is advisable on all accounts to sow on the flat with 40 : 20—25 cm., and on the ridge distance 45 : 20—25, and the highest results, both yield and sugar, are obtained by sowing on the ridge by Bertel's method, which consists in throwing up ridges 44 cm. apart, rolling them, and employing a combined manure and turnip drill.

E. W. P.

**Ammonia in Rain-water.** By HOUZEAU (*Bied. Centr.*, 1883, 425).—The principal agents which increase or diminish the amount of ammonia are light and heat. In July the observer was not able to detect even a trace of it in rain-water. He found that water exposed to the action of sunlight for a long time lost a large part of its ammonia. The amount of rainfall also has an influence; the smaller the amount the more ammonia it contains.

J. F.

**Origin of Combined Terrestrial Nitrogen.** By A. MÜNTZ and E. AUBIN (*Compt. rend.*, 97, 240—243).—The principal source of combined nitrogen appears to be nitric acid and oxides of nitrogen, formed by the action of atmospheric electricity on the nitrogen in the air. The main causes producing a diminution in the amount of combined nitrogen are, rapid combustion, which operates only to a limited extent; slow combustion, which is the most important cause of all; and the reduction of nitrates in water and soils, which plays a very insignificant part. In order to ascertain whether these increasing and diminishing forces are in equilibrium, it is necessary to determine the amount of nitric acid in the rain-water on different parts of the earth's surface, and especially in tropical regions. The accurate estimation of nitrates can be performed only in a properly appointed laboratory, and it is advisable therefore, to collect the samples of rain-water in such a way that they can be transported to a distance. The authors recommend to evaporate the rain-water to small bulk with potassium hydroxide, out of contact with air and products of combustion. The concentrated liquid is mixed with alcohol, and the authors find that in this condition it may be preserved for any length of time without undergoing any alteration. To apply this method to river water, &c., 3—5 litres of the water are evaporated to about 30 c.c., and mixed with 60 c.c. of alcohol.

Many cases of rapid combustion are accompanied by the formation of considerable quantities of nitric acid. The authors find that when 1 gram of hydrogen burns in air, 0.001 gram of nitric acid is produced, whilst the combustion of 1 gram of magnesium is accompanied by the formation of 0.1 gram of nitric acid. It is probable, therefore, that a large quantity of nitrates were formed in the earlier stages of the earth's history during the process of cooling, and the luxuriant development of animal and vegetable life in prehistoric times was possibly due to the presence on the earth's surface of a large quantity of combined nitrogen in an assimilable form. It would appear, therefore, that the total amount of combined terrestrial nitrogen is gradually



diminishing, unless the sources of loss are balanced by the action of atmospheric electricity. C. H. B.

**The Lupitz Method of Cultivation.** By SCHULTZ and others (*Bied. Centr.*, 1883, 232—243).—Schultz considers that the cultivation of lupines is the cheapest method of supplying the soil with nitrogen, as they abstract this constituent from the air. According to his experiments a soil in which lupines had grown showed an amount of nitrogen double that in grass land, and more than that found in potato and rye land. According to Schultz all that is necessary for a good crop of lupines is the addition of kainite; phosphates do not give a satisfactory result. Drechsler criticising Schultz's statements, shows that lupines do not add nitrogen to the soil, but rather, like all large-leaved crops, even when they draw their supplies of nitrogen from the subsoil, are consumers of nitrogen instead of collectors, and he also considers that the Lupitz system, unless nitrogen is added to the land, cannot last. Blomeyer's opinion is that the leguminosæ are "nitrogen collectors," and for this reason, that they keep the surface of the soil moist, and so prevent the volatilisation of ammoniacal compounds. Märcker is unable to answer the question whence the excess of nitrogen which is present in the Lupitz soil is derived, for 675 lbs. N have in 15 years been withdrawn, and only that nitrogen added from the usual natural, viz., the atmospheric, not artificial sources. It is possible that the deep rooting lupines may separate nitrogen from solutions which are too dilute for other plants, and the retention of nitrates on the surface soil may be due to the shelter afforded by the foliage, preventing loss by rainfall. He believes that by the continued use of kainite the nitrogen in time will be lost, and that though phosphates are now useless, they will hereafter be required; in the 15 years 1000—2000 kilos. lime per hectare have been removed, by reason of the potash manure, so that this constituent will before long be required. Märcker believes that potassium chloride as carnallite is a better manure than the sulphate as kainite.

E. W. P.

**Moss and Turf Fibre as Cattle Litter.** By M. FLEISCHER and others (*Bied. Centr.*, 1883, 368—373).—The use of so-called "moss litter" obtained from certain bogs in Northern Germany has become very general. The authors of this paper have examined samples of ordinary fibrous peat, separated artificially, and intended as substitutes for the former, one sample procured from Württemberg, the other from a Silesian bog. They found that air-dried samples containing 20 per cent. of moisture, absorbed  $6\frac{1}{3}$ — $9\frac{1}{2}$  times their weight of water, and their power of absorbing carbonate of ammonia for 1000 parts of moss, 13—16 parts of ammonium carbonate.

The manurial value of the different samples is given. 1000 parts of each contain—

	Württemberg fibre.	Silesian fibre.	North German moss.
Nitrogen . . . . .	22.0 parts	29.0 parts	9.0 parts
Phosphoric acid..	0.6 "	0.6 "	0.4 "
Lime . . . . .	17.2 "	31.0 "	2.0 "

The two samples of fibrous turf are consequently much more valuable as manure than the moss; and containing much lime, their nitrogen is probably more readily decomposed, and available for plant nutrition.

Analysis of turf fibre employed as absorbents in public and private middens in Bremen, and in horse stables, yielded the following results, calculated to 1000 parts of the dry substance:—

	Public latrines.	Private latrines.	Stables.
Nitrogen.....	46·6	27·8	17·3
Mineral matters..	118·8	?	167·0
Potash.....	23·3	9·3	7·9
Phosphoric acid..	18·7	10·6	7·0

The samples were free from smell, and although containing a considerable amount of moisture, formed a compact and portable mass.

The remainder of the paper is occupied with experiments on various crops with the moss after being used as litter, and in all cases the results were satisfactory. J. F.

**Sea Mud.** By M. FLEISCHER, A. KONIG, and B. KISSLING (*Bied. Centr.*, 1883, 243—250).—Mud is deposited at the mouths of most rivers, which it is advantageous to the harbour authorities and to the farmer to remove. Analyses show that with but slight variation the deposits are of the same composition, the principal variant being sand. This mud when exposed to the air dries to a firm compact and plastic mass, and at the same time that it loses water, it also diminishes in volume; in one case the ratio of loss of water to loss of volume was 1 : 0·55. The changes effected by long storage are of considerable importance to the agriculturist, for the physical character changes, the mud becoming more pulverulent, and consequently more easily applied to the land, and this is especially the case after frost; also water being lost and volume reduced, transport expenses are lowered, chlorides are lost, ferrous oxide and sulphide become oxidised, plant and animal remains become more decomposed, and but little, if any, nitrogen is lost. Further changes are induced by frost and thawing, for the dry matter is raised from 45·6—65·06 per cent., and the whole becomes still more friable, and a higher percentage of soluble sulphate and lime is obtained. E. W. P.

**Destruction and Utilisation of the Bodies of Animals which have Died from Contagious Diseases, especially from Anthrax.** By A. GIRARD (*Compt. rend.*, 97, 74—77).—The body, without removal of the skin, is dissolved in the cold in concentrated sulphuric acid of about 60°. Complete solution takes place with comparative rapidity, and the acid can be used repeatedly until its degree of concentration is diminished to 43°. Direct experiments have proved that all germs are destroyed in the process of solution. The acid liquid obtained contains a considerable proportion of nitrogen, and has the power of readily attacking natural phosphates yielding highly nitro-

genous superphosphates. A layer of fatty matter floats on the surface of the acid solution, and may be removed and purified.

C. H. B.

**Guano recently discovered in Australia.** By A. B. GRIFFITHS (*Bied. Centr.*, 1883, 427).—The following is the analysis of two samples:—

	No. 1.	No. 2.
Nitrogenous organic matter		
and ammoniacal salts ....	46.72	46.73
Phosphoric acid .....	15.02	15.10
Lime .....	18.00	17.99
Alkaline salts .....	1.42	1.41
Sand ....	2.71	2.71
Water .....	15.92	16.07
	<hr/>	<hr/>
	99.79	100.01

J. F.

**Manurial Value of Sewer Slime.** By M. FLEISCHER (*Bied. Centr.*, 1883, 426—427).—In Bremen several sewers connected with houses, and containing much urine, are led into a small stream with a gentle fall; the solids precipitate, and are removed for agricultural purposes. An analysis of a sample yields the following:—

	Dry.	With 45 per cent. of water.
Potash.....	6.3	3.5
Lime .....	17.2	9.5
Phosphoric acid .....	8.0	4.4
Total nitrogen.....	11.6	6.4

The reaction is acid, and it contains soluble iron salts; ignited in a platinum capsule sulphurous acid is evolved. The wet material when heaped up yields a drier mass of 50—60 per cent.; it must be exposed a long while to the air in consequence of the sulphur compounds.

Another sample drawn from a pond into which the night soil from a part of the city was for a long time allowed to flow. This sample also gave an acid reaction. The addition of hydrochloric acid causes evolution of sulphuretted hydrogen.

This sample yielded in 1000 parts—

	Fresh.	Dried at 100°.
Water .....	889.70	—
Combustible matter ..	27.20	251.0
Nitrogen .....	1.46	13.2
Insoluble in HCl.....	54.25	498.8
Potash .....	0.98	8.9
Soda.....	0.34	3.1
Lime.....	1.91	17.3
Magnesia .....	1.35	12.2
Iron and alumina ....	18.25	165.5
Phosphoric acid .....	0.52	4.7
Sulphuric acid .....	3.65	33.1

J. F.

**Constituents and Properties of some Water Plants.** By NIEDERSTADT (*Landw. Versuchs.-Stat.*, **29**, 247—250).

*Stratiotes aloides*.—The use of this as manure has been followed by exceedingly good results, better in fact than with any other ordinary manure. Analysis of the ash shows that it is very rich in alkalis and phosphates. It contains 19·5 per cent. of ash, and 15·7 per cent. protein. In the ash was found 14·2 per cent. soda, 15·9 per cent. potash, and 11·4 per cent. phosphoric acid.

*Nymphaea alba*.—The leaves of this plant yielded 11·1 per cent. of ash, consisting chiefly of alkaline chlorides and calcium carbonate, and the same may be said of the ash of the leaves of *Nuphar luteum*. The flowers of these plants contained large quantities of chloride and phosphate of potassium. J. K. C.

**Kainite as Potato Manure.** By M. FLEISCHER (*Bied. Centr.*, 1883, 366—367).—These experiments were made at the instance of the Central Moor Commission, in order to learn the effects of early and late applications of kainite to potatoes. Four plots were manured with precipitated phosphate and Chili saltpetre; to one no potash salt was applied; No. 2 received kainite in September; No. 3 kainite in December, and No. 4 immediately previous to planting, the effect of the kainite was remarkable, the average of the crop taken off the three plots on which it was used, being three times as great as that from the other plot. The yield of the three plots treated with kainite was nearly alike, but the flavour of the September manured plot was best; the yield of starch, however, determined by König's sp. gr. method, was:—

September plot.	December plot.	At sowing.
100	67	64

Similar experiments were made by Wildt in 1882. The time of applying the kainite did not appear to affect the gross weight of the crop, but the starch percentage was greatly diminished by late applications. When the kainite was applied at the under-mentioned periods the net yield of starch and its proportion, taking the highest figure as 100, were:—

	Autumn.	Early spring.	Four weeks before planting.	At planting.
Centner ..	20·9	18·8	18·1	17·5
	100	90	87	84

The author ascribes the loss of starch to the presence of chlorides. J. F.

## Analytical Chemistry.

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**Estimation of Chlorine, Sulphuric Acid, and Chromium in Presence of Organic Matter.** By C. T. POMEROY (*Chem. News*, 48, 41—42).—To determine these substances in the presence of organic matter, it is first of all necessary to remove the latter by ignition with an alkaline carbonate and nitrate; some of the nitrate is thereby reduced to nitrite, which, during subsequent operations, reduces the chromates, and interferes with the estimation of chlorine; moreover, if the sulphuric acid is precipitated in this solution, the barium sulphate always retains chromic oxide. To obviate these difficulties the mass from the fusion with alkaline carbonate and nitrate is dissolved and filtered; potassium nitrite and nitric acid in excess are added to the filtrate, which is allowed to stand 12 hours in the cold. On adding ammonia and boiling, the chromium hydroxide is thrown down; it should be filtered off hot, washed with hot water, and estimated as usual. The sulphuric acid is precipitated from the filtrate from the chromium hydroxide by means of barium nitrate, and the chlorine estimated in the filtrate from the barium sulphate in the usual way. The published results agree very well. In the analysis of ordinary chrome yellow, even the lead passes entirely into solution when sufficient sodium nitrite and nitric acid are added, and the mass boiled.  
D. A. L.

**Formation of Methylene-blue as a Reaction for Hydrogen Sulphide.** By E. FISCHER (*Ber.*, 16, 2234—2236).—To test for hydrogen sulphide in aqueous solution, the latter is treated with one-fiftieth volume of concentrated hydrochloric acid, a few grains of paramidodimethylaniline sulphate are added, and when this is dissolved, 1—2 drops of a dilute solution of ferric chloride. In the case of a solution containing 0.00009 gr. hydrogen sulphide in a litre of water, coloration took place in a few minutes, and in half an hour the liquid had assumed a strong blue colour, which lasted for days. A solution of the same strength, but without hydrochloric acid, yielded only a light brown coloration with lead acetate. In a solution containing 0.0000182 gr. hydrogen sulphide in a litre of water, the methylene-blue reaction still gave a distinct blue coloration, whilst no effect was produced either by lead acetate or sodium nitroprusside. This reaction is recommended as the most delicate and certain test for neutral or acid solutions of hydrogen sulphide. Paramidodimethylaniline is most conveniently prepared from commercial helianthin,  $\text{Me}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$ ; this is finely powdered, mixed with 5 parts of water and an excess of ammonium sulphide; the mixture is frequently agitated, and when (after about 24 hours) the reduction is complete the amidodimethylaniline can be extracted with ether; the ethereal solution is then agitated with a little white lead suspended in water, and the filtrate treated with an ethereal solution of concentrated sulphuric acid. The ether is separated from

the crystalline sulphate, and this is heated with absolute alcohol until it is converted into slender white needles, which after being washed with alcohol can be pressed and dried on a water-bath.

A. K. M.

**Volumetric Estimation of Phosphoric Acid.** By G. C. CALDWELL (*Chem. News*, 48, 61—62).—The author finds Pemberton's method (*Abstr.*, 1882, 1318) efficient; he has introduced an improvement to facilitate the final test filtrations. A test-tube is fitted with a double-bored cork, through which pass two tubes, a short one bent at right angles and a longer one bent at a convenient angle for introduction into a beaker; the bore of the tube is 1 mm., the end of the longer one has a conical enlargement or mouth with a diameter of 5 mm. To prepare the apparatus for use a perforated platinum cone is fixed in this mouth, and while suction is applied to the short bent tube, the mouth of the tube with the cone is just dipped into very thin asbestos pulp and then into water, the suction being continued until the water comes through quite clear. The apparatus is now ready for use; suction is again applied, the filter dipped into the liquid to be tested, and when the desired quantity of filtered solution is obtained, the filter is withdrawn; the suction must be sustained all the time to prevent the cone and asbestos from falling out. The liquid is treated in the test-tube, and then returned to the beaker. Before the next test is made the filter and tube are washed by a small quantity of the liquid, which is drawn through the filter and returned to the beaker.

D. A. L.

**Quantitative Separation of Potash and Soda from Ferric Oxide, Alumina, Lime, and Magnesia in Silicates.** By W. KNOP (*Chem. News*, 48, 110—111). The new method is based on the formation of alkaline silicofluorides insoluble in acidulated mixtures of alcohol and ether, by the combined action of hydrochloric and hydrofluoric acids on silicates. When the alkalis are in excess it is necessary to add silica before treatment with the acids.

The weighed substance, mixed with a small quantity of water, and, if necessary, silica also, is treated, in a platinum capsule, with fuming hydrofluoric acid, evaporated to dryness, treated with strong hydrochloric acid and absolute alcohol, and after some time with excess of ether. In 12 hours' time the silicofluorides are filtered off, washed with alcohol, dried, and removed from the filter, which is incinerated. The ash and the precipitate are mixed together in a crucible with concentrated sulphuric acid, and as soon as the evolution of silicon fluoride ceases the crucible is ignited at a low temperature, so as to leave the alkalis as acid sulphates. The mass is treated with ammonia, evaporated to a paste, rendered alkaline with ammonia, and after an hour, to ensure complete separation of iron and alumina, is treated with ammonium carbonate solution and left for 12 hours. The iron, alumina, lime, and magnesia, are filtered off and washed with ammonium carbonate, &c. The filtrate is evaporated to dryness—a quantity of ammonium hydrogen tartrate equal to the ammonium sulphate present being added to prevent spurting—and ignited. The

residue is taken up with water, tested with ammonium carbonate for iron, &c., and the solution is then evaporated to dryness and weighed.

D. A. L.

**Methods of Analysing Columbates by means of Hydrofluoric Acid. Separation of Thoria from the other Oxides. Estimation of Didymium.** By J. L. SMITH (*Chem. News*, 48, 13—15; 29—31).—After a review of the work done on this class of minerals by Rose, Hermann, Marignac, &c., the author observes that they have special interest, because there are always some of the rarer earths associated with them, and the reasons amongst others which have prevented their being more perfectly studied are, firstly, the scarcity of the minerals, and secondly, the difficulty attached to the process of decomposing them. The first obstacle was removed by the discovery of large quantities of columbite and samarskite in the United States, and the second is set aside by the methods described in this paper.

In a previous communication (*Amer. J. Sci.*, 1877, 360), the author has described these minerals, columbites and tantalites from the United States, both as regards their mineralogy and their chemical composition, but owing to the defects in the manner of working, he could neither give the relative proportions of columbic and tantallic acids, nor could he detect conclusively cerium or thorium. All doubt on this head has been dispelled by the use of his new method.

*Analysis of Samarskite (and other Columbates containing Earthy Oxides).*—5 grams of the finely powdered mineral dried at 150° (loss by ignition is determined in a separate quantity) are placed in a platinum capsule (50 c.c. capacity is sufficiently large) moistened with water and treated with 4 to 5 c.c. of concentrated hydrofluoric acid; after two or three minutes, a second and similar quantity of this acid is added, and the whole well stirred; vigorous action soon sets in, and in 5 or 10 minutes all black specks have disappeared, showing the decomposition to be so far complete. The capsule is now heated on a water-bath; the contents consist of a clear *solution* (A) containing the metallic acids, iron and manganese, and an *insoluble portion* (B) containing the earths and uranium oxide. These two parts are but very slightly intermixed. The contents of the capsule are mixed with 30 c.c. of water, warmed, filtered on a gutta-percha or silver funnel, the filtrate being received in a platinum capsule, and washed with hot water containing a few drops of hydrofluoric acid. The *solution* is evaporated over a water-bath, and before it is dry, is treated with excess of concentrated sulphuric acid to decompose the fluorides; it is heated until nearly all the sulphuric acid is driven off, and when cool is washed into a glass flask and boiled with very dilute hydrochloric acid. The whole mass is then filtered and washed with hot water. The precipitate, consisting of columbic, tantallic, and small quantities of tungstic and stannic acids is dried, ignited and weighed; subsequently the tungstic and stannic acids are separated in the manner recommended by Rose, and the columbic and tantallic acids by Marignac's method. The filtrate contains iron and manganese, which are estimated in the usual manner. The *insoluble portion* is washed into a platinum capsule, treated with a sufficient quantity of concentrated sulphuric acid to decompose the fluorides, heated carefully until nearly

all the sulphuric acid is driven off, and when cool is warmed with 50 c.c. of water, in which all dissolves to a green solution, except perhaps a very minute quantity belonging to portion A. The green solution is heated, and after the addition of a little nitric acid, is poured into a beaker and made up to about 250 c.c. with water. It is now nearly neutralised with ammonia, and the earths precipitated with ammonium oxalate or oxalic acid. After six or eight hours, the *earthy oxalates* (C) are filtered off and washed. The solution contains all the uranium with a trace of iron; both are estimated; the iron is precipitated as sulphide, and the uranium estimated by the ordinary method. The *earthy oxalates* are dried, ignited, and weighed. The powder, which is of a pale yellow colour, is dissolved in nitric acid, evaporated to a syrup, and before it solidifies is mixed with a concentrated solution of sodium sulphate, and subsequently small crystals of the sulphate are added (50 c.c. of the solution and 4 grams of the crystals for 1 or 2 grams of mineral), a precipitate (D) soon begins to form. After 24 hours it is very abundant and is filtered off and washed with concentrated sodium sulphate solution. The filtrate containing yttrium and erbium is treated with oxalic acid or ammonium oxalate, the precipitated oxalates ignited, redissolved, reprecipitated, ignited, and weighed. The oxides are dissolved in dilute sulphuric acid, evaporated carefully, and heated until the weight is constant: then from the weight of oxide and of sulphate, the relative proportion of yttria and erbia is found by Bahn and Bunsen's formula. The sodium sulphate precipitates are separated by fractional precipitation; they are washed with solution of the salt, dissolved in very diluted hydrochloric acid, nearly neutralised with ammonia, precipitated by ammonium oxalate, ignited, redissolved, reprecipitated, and weighed.

No cerium was found in the first precipitate, but instead a dark oxide soluble in very dilute nitric acid, which the author called mosandrum oxide. In the precipitate D are found the other cerium oxides and thorium. After being treated in the usual manner with hydrochloric acid, ammonia, oxalic acid, &c., and ignited, the resulting oxides dissolved in dilute nitric acid, thus again showing absence of cerium oxide. This fact was now confirmed by treating the nitric acid solution with caustic soda and chlorine, no indications of cerium were obtained, all the oxides passing into solution with the exception of a small quantity of thorium, which forms 0.8 per cent. of the mineral. Some experiments were now conducted on a large scale, lead vessels, capable of working more than a kilo. of mineral at a time, were employed instead of platinum ones. The conduct of the process is the same as described above, the earthy fluorides are decomposed with sulphuric acid, &c., and after the separation of uranium oxide, &c., the solution is boiled up with steam, nearly neutralised, and the oxalates precipitated. The yttria is separated as above described; the thorium can be separated quantitatively by treating the solution with large quantities of soda and passing chlorine for two or three hours as above described, or less completely by dissolving the earths, separated by the sodium sulphate, in nitric acid, concentrating the solution on a water-bath, diluting abundantly, boiling with a current of steam, and adding sufficient ammonia to the boiling solution to precipitate about  $\frac{1}{8}$



of the oxides present. The gelatinous precipitate containing all the thoria and a little of the other oxides, is filtered off, washed, and dissolved in dilute sulphuric acid; this sulphate of thoria can be easily purified by the usual methods. The filtrate from the thoria contained a mere trace of thoria, and no lanthanum, therefore the only oxide of the cerium series to be looked for was didymium, which the author recognised by the spectroscope.

*Quantitative Estimation of Didymium.*—Solutions of didymium oxide of known strength are placed in tubes of uniform diameter, these are compared before the spectroscope with similar tubes containing a nitric acid solution of the oxides to be tested, until the bands produced by the tubes correspond in intensity; the author in this manner arrived at the quantity of didymium in solution. From these results it is evident that the samarskite examined by the author contained thoria, and other mixed oxides in place of the cerium oxide.

Columbite and tantalite are more difficult to decompose than samarskite. They must be very finely pulverised; to effect this with tantalite, the powder in the mortar is covered with (95 per cent. commercial) absolute alcohol, and the trituration continued under these circumstances. The trituration of 1 gram of columbite requires a quarter of an hour; 1 gram of tantalite 20 minutes. They are then decomposed by heating with hydrofluoric acid of the usual strength used by the author, and treated as described above. D. A. L.

**Dialysis of Arable Land.** By A. PETERMAN (*Bied. Centr.*, 1883, 361—364).—The employment of strong mineral acids in the analysis of soils has led the author to think that substances pass into solution and are estimated, which under the ordinary conditions of cultivation are not attacked, and are useless to the plant. He has, therefore, tried a system of dialysis with distilled water, which he believes follows better the processes of nature. The dialyser employed was somewhat, but not materially different from the ordinary apparatus. It was found that after a dialysate of 10 days, not only the soluble salts but a notable proportion of organic matter had passed into the distilled water, colouring it yellow, yielding a dark brown residue after cautious evaporation, and a carbonaceous residue on ignition. This substance is different from the *matière noire* of Grandeau, which does not pass through parchment-paper. The author refers to old experiments of Risler made in 1858, showing that plants derive a portion of their carbon from the soil, and not entirely from the atmosphere.

J. F.

**Titration of Copper by Means of Potassium Cyanide.** By J. J. and C. BERINGER (*Chem. News*, 48, 111—113).—The authors have studied some of the conditions which affect the accuracy of this method for the determination of copper, and publish the results, &c., in this paper.

*Effect of Manner of Working.*—The result is not so much affected by the time occupied in the entire titration as it is by the rate with which the last 2 or 3 c.c. are run in. The manner of finishing is, therefore, of paramount importance; and in order to obtain concordant results, a fictitious finishing point must be adopted.

*Effect of Variations of Temperature.*

Temperature in C.	10°.	20°.	30°.	47°.
c.c. Cyanide required .....	23·5	23·3	23·05	22·85

*Effect of Ammonium Salt.*

	Without.	With chloride.	With sulphate.	With nitrate.	With carbonate.
c.c. Cyanide required ..	24·2	25·7	25·7	25·6	25·6
Do. in presence of soda..	25·6	26·75	26·7	26·75	26·4

*Effect of Quantity of Ammonia.*

c.c. Ammonia added..	0	2	5	10	20	30	50	100
c.c. Cyanide required..	21·8	22·5	22·8	33·0	23·3	23·4	23·7	24·2

*Effect of Quantity of Ammonium Nitrate.*

Grams AmNO <sub>3</sub> .	0	1	2	4	12
c.c. Cyanide required..	24·2	24·6	25·0	25·4	26·5

*Effect of Alkali Salts.*

—	Without.	With sodium sulphate.	With chloride.	With nitrate.
c.c. Cyanide required.	24·9	24·90 25·05 25·10	24·95 25·00 25·10	24·90 24·90 24·95

*Effect of Soda.*

c.c. Soda.	0	1	5	10	20	50
c.c. Cyanide required ..	25·8	26·0	26·4	26·9	27·25	28

It is evident that sodium salts are less objectionable than ammonium salts; and by neutralising with soda instead of ammonia, ammonium salts are avoided. Therefore if only a slight excess of soda be employed, whilst the temperature and mode of working are the same, the present question is greatly simplified, the only matter to be considered being the effects of the relative quantities of reagents :

these may be summed up thus; when the copper, ammonia, and volume of liquid vary, but retain their relative proportions, the quantity of cyanide used is proportional to the copper present. If, however, the copper and volume are constant, whilst the ammonia increases, more cyanide is required. On the other hand, if the ammonia and copper are constant, whilst the bulk increases, less cyanide is necessary. Hence the authors inferred that by adding water and ammonia in proper proportions these errors might be got rid of. They have employed successfully 15 c.c. of 0.880 ammonia to each 300 c.c. of liquid, in slightly alkaline solution, titrating with the necessary precautions.

D. A. L.

**Colorimetric Estimation of Gold.** By A. CARNOT (*Compt. rend.*, **97**, 169—170. (See below.)

**New Reactions of Gold.** By A. CARNOT (*Compt. rend.*, **97**, 105—108).—A dilute solution of auric chloride is mixed with a small quantity of arsenic acid, two or three drops of ferric chloride solution, and the same quantity of hydrochloric acid diluted with 100 c.c. of water, and a fragment of zinc are added. A purple colour is soon developed in the neighbourhood of the zinc, and on agitation the liquid acquires a rose or purple tint. The same colour is also immediately produced if, instead of zinc, the solution be mixed with a few drops of an acid solution of ferrous chloride, or of the solution obtained by acting on metallic iron with arsenic and hydrochloric acids. This reaction succeeds with less than 0.0001 gram of gold in 100 c.c. of water. With phosphoric acid in place of arsenic acid, a violet or bluish coloration is obtained. Hydrochloric acid alone gives a less intense rose coloration. Hydrogen gas, mixed with small quantities of hydrogen sulphide, may be used instead of zinc or ferrous chloride.

The rose or purple liquid is perfectly transparent, can be filtered without being decolorised, and is unaltered at the end of three months. It is, therefore, a true solution, and is not a liquid holding finely-divided gold in suspension. If the solution is not distinctly acid, or if it be mixed with certain salts, especially ammonium salts, a flocculent purple precipitate is slowly deposited. If the liquid is too acid, the reaction does not take place, but finely-divided gold is precipitated. The same decomposition occurs if the reducing agent is added too rapidly, or if the precipitate, when once formed, is redissolved in hydrochloric acid. If the reducing agent is added gradually, a considerable excess appears to have no action on the rose or purple compound. The precipitate has a composition corresponding with the formula  $\text{Au}_2\text{O} \cdot 19\text{Fe}_2\text{O}_3 \cdot 15\text{AsO}_5$ . It would appear, therefore, that the action of the reducing agent is only partial, aurous oxide and ferric oxide being formed. The ferric chloride, the presence of which is essential, in all probability acts as a restrainer of the reducing action.

C. H. B.

**Estimation of Arsenic: Pearce's Process.** By O. J. FROST (*Chem. News*, **48**, 85—86. Compare *Abstr.*, 1883, 1034—1035).—In this process, the finely-powdered substance is fused with six to ten times

its weight of the sodium carbonate and potassium nitrate mixture and then proceed as described (*loc. cit.*), the solution, however, instead of being evaporated to dryness, is exactly neutralised with ammonia and nitric acid, and filtered, if necessary. Excess of neutral silver nitrate solution is now added; the silver arsenate filtered off and washed with cold water, and the filtrate tested to see that precipitation is complete. The amount of silver is determined and the arsenic calculated from it. This is best effected by dissolving the arsenate on the filter in dilute nitric acid (any chloride is thus left behind), and titrating the filtrate for silver, with thiocyanate. Good results have been obtained by this method, which the author states can be worked in half an hour. Molybdic and phosphoric acids interfere with the process; antimony does not, on account of the insolubility of sodium antimonate.

D. A. L.

**Volumetric Method for the Estimation of Arsenic.** By A. H. Low (*Chem. News*, 48, 85).—A defence of Pearce's process (see last abstract) against some criticisms made by McCay. The author considers that dissolving the precipitated silver arsenate in dilute nitric acid and titrating the silver is better than determining the excess of silver as McCay does (*Abstr.*, 1883, 1035), for any chlorine present as impurity in the reagents would have no effect in the first case, because any silver chloride present would not be dissolved, but would lower the results in the latter method. He also recommends the use of a platinum instead of porcelain crucible for the fusion, as it can be more easily cooled, and, from experience, he states that it remains apparently uninjured, even after many times using.

D. A. L.

**Test for Bismuth Subnitrate.** (*Dingl. polyt. J.*, 248, 260).—According to Hager, bismuth subnitrate and bismuth subarsenate dissolve in eight parts of nitric acid of sp. gr. 1.185, forming clear solutions; the latter is, however, not completely soluble in a solution saturated with bismuth nitrate. Hence, by treating 0.5 gram of the subnitrate with 4 grams nitric acid, a clear solution should be obtained within half an hour, otherwise arsenate is present.

D. B.

**Estimation of Manganese in Iron Ores.** (*Dingl. polyt. J.*, 248, 259).—Zulkowsky recommends incineration of the manganous sulphide precipitate in a platinum capsule, and moistening the residue with aqueous sulphurous acid. The solution is evaporated on a water-bath, the residue taken up with water and two to three drops of dilute nitric acid, and titrated with potassium permanganate. For this purpose, the solution is transferred to a flask, diluted with water to 150 to 200 c.c., and boiled. To the hot solution, potassium permanganate is added from a burette, and the mixture boiled after each addition until the supernatant liquid shows a pale red colour. According to the formula  $3\text{MnO} + \text{Mn}_2\text{O}_7 = 5\text{MnO}_2$ , 1 c.c. of a decinormal solution of potassium permanganate corresponds with 1.65 mgrm. manganese.

D. B.

**Volumetric Method of Estimating Manganese, especially in Iron and Steel.** By R. SCHÖFFEL and E. DONATH (*Dingl. polyt. J.*, 248, 421—424).—To conduct this method, a solution of sodium car-

bonate is required, which does not reduce potassium permanganate even on boiling; also a solution of potassium permanganate of known strength. For this purpose sodium hydrogen carbonate is converted into the normal carbonate by strongly heating it. A saturated solution of the carbonate is then prepared, which is heated to boiling and treated with a solution of potassium permanganate until the mixture assumes a faint reddish colour, which remains on continued boiling. The fluid is kept in well-stoppered bottles, and although its colour soon disappears, it no longer affects potassium permanganate. The solution of potassium permanganate is titrated with pure iron wire or with ammonium ferrous sulphate. As this reaction is illustrated by the equation  $10\text{FeO} + \text{Mn}_2\text{O}_7 = 5\text{Fe}_2\text{O}_3 + 2\text{MnO}$ , and the equation which explains the action of potassium permanganate on the manganese salt is  $3\text{MnO} + \text{Mn}_2\text{O}_7 = 5\text{MnO}_2$ , 10 atoms of iron correspond with 3 atoms of manganese; so that by multiplying the iron value by 0.2946, the permanganate value is obtained.

For the analysis of samples rich in manganese, such as pig iron, spiegeleisen, and ferromanganese, 2 to 1 grams,—for poorer samples, 4 to 3 grams,—are dissolved in boiling hydrochloric acid. The mixture is allowed to cool, treated with a small amount of potassium chlorate, and again boiled until all chlorine has been expelled. The solution, if too acid, is evaporated to a small bulk, partly neutralised with sodium carbonate, and made up to 100 c.c. 50 to 60 c.c. of the solution of sodium carbonate are then transferred to a flask holding 700 to 800 c.c., diluted with 400 to 500 c.c. distilled water heated to boiling, and treated with standard potassium permanganate. The test solution is then run in from a burette, the mixture being stirred all the while. From the instant the colour becomes fainter, the solution should be added with caution, and the mixture allowed to settle from time to time. The operation is concluded as soon as the red colour of the fluid has disappeared. The amount of permanganate solution used should be so regulated that one-half, or at least one-third of the test solution is required, otherwise the results will be vitiated too much by the limits of error.

D. B.

**Suspended Matter in Water.** By E. MARCHAND (*Compt. rend.*, 97, 49—50).—The water under examination is placed in a flask surrounded by black paper, in which are cut two opposite rectangular apertures, and a beam of light is passed through the water. This method of examination reveals the existence of a large number of suspended particles which are invisible under ordinary conditions, but which the author has found to exist in large numbers in all forms of natural water, and even in distilled water which has been exposed for some time to the air. Some of these particles are vacuoles containing water or gas, others have a shape resembling that of discoidal diatoms. They have a sp. gr. higher than that of sea-water (in which they are very abundant), and they are not attacked by dilute acids or alkalis. Amongst these suspended corpuscles are germs of *Euglena*, a fact which explains the development of green growths in all places exposed to light and moisture, and they also include organisms which probably play an important part in the oxidation of the organic

matter contained in water. Although some of them have a diameter as great as 2 mm., they are so flexible that they pass through the closest filters, and when taken into the body they can pass through the kidneys, and are found in the urine. C. H. B.

**Test for Glycerol and Woody Fibre** (*Dingl. polyt. J.*, 248, 259).—According to Reichl, minute quantities of glycerol can be detected by boiling the solution to be examined with a small amount of pyrogallol and a few drops of sulphuric acid diluted with an equal volume of water; this causes the formation of a red colour, which is changed to purple on adding stannic chloride. Carbohydrates and certain alcohols must be absent, as they produce similar colours. By boiling woody fibre in a solution of stannic chloride mixed with a few drops of pyrogallol, a fine purple colour is formed. This reaction can be used as a means of dyeing wood. D. B.

**Valuation of Sugar-beets by their Density.** By A. v. WACHTEL (*Bied. Centr.*, 1883, 421—422).—The custom of valuing beet-roots by their weight is a rough and ready rule; the beet-juice on analysis frequently shows considerable differences. The author recommends Krockner's process, that is, to prepare several mixtures of calcium chloride or cane-sugar solutions of different sp. gr., then with a sampling tool to take pieces out of the root, placing them in solutions of different densities until they float. Considerable differences are caused by the manner in which the roots are cleansed for sampling, roots which are brushed and wiped showing a greater percentage of sugar than those cleaned with warm water. J. F.

**Detection of Silver Cyanide.** By C. L. BLOXAM (*Chem. News*, 48, 49).—The following test is of use in qualitative work. Precipitated silver cyanide appears amorphous under the microscope; if, however, it is treated with ammonia and warmed, it forms needles. Silver chloride, treated in similar manner, forms octohedrons. In a mixture of the two, both constituents can be recognised in this way. Silver thiocyanate also forms needles under like conditions, the absence of thiocyanic acid must therefore be ascertained by the iron test. Silver cyanide also crystallises when boiled with a strong solution of sodium carbonate, or when moistened with strong nitric acid and warmed. Silver cyanide can be separated from silver chloride by treating the mixture with hot dilute nitric acid in which the cyanide is soluble. If the solution is cooled, and the tube containing it is kept still, the cyanide separates in a semi-transparent gelatinous form; if, however, the tube is agitated, the precipitate collects suddenly into opaque masses (generally) of microscopic needles. D. A. L.

**Reactions with Silver Cyanide, Ferrocyanide, and Ferricyanide.** By C. L. BLOXAM (*Chem. News*, 48, 73—74).—When white silver ferrocyanide is shaken with ammonia it forms an opalescent liquid. When heated it becomes brownish-grey in colour, and metallic silver is deposited. When treated with nitric acid, the grey precipitate yields a solution of silver nitrate and ferric nitrate, leaving

a residue of ferric oxide, mixed with a little silver ferricyanide. No cyanide could be detected in this precipitate by means of ammonium sulphide. With hydrochloric acid, a solution containing both ferrous and ferric chlorides is obtained.

The ammoniacal solution neutralised with nitric acid yielded silver and ammonium cyanide. When silver ferrocyanide is treated with a cold strong potash solution, a heavy brown precipitate forms. The supernatant liquid is colourless, stains paper brown, and on being heated deposits silver; it contains a trace of potassium cyanide, but no ferrous or ferri-cyanide. The brown precipitate contains metallic silver, and silver ferro- and ferri-cyanide. Apparently, then, a part of the silver ferrocyanide is converted into ferricyanide with separation of silver; and the ferricyanide thus formed forms a compound with the unchanged ferrocyanide, which compound is not decomposed by cold potash or warm ammonia. Boiling with potash entirely decomposes the ferrocyanide, yielding a solution of potassium and silver cyanide, and leaving a residue of ferrous and ferric oxides and silver. By boiling together precipitated silver oxide, silver ferrocyanide, and water, the colour changes from brown to black, and silver and silver cyanide and ferricyanide are produced. When silver ferricyanide is treated with potash in the cold it becomes black, yielding silver oxide and potassium ferricyanide; on boiling, the black precipitate changes to pink, and ammonia is evolved, but on continuing to boil the precipitate again becomes black. The pink precipitate contains a compound of silver cyanide with silver ferricyanide insoluble in ammonia, along with silver cyanide, silver ferrocyanide, and ferric oxide. The pink precipitate can be exactly reproduced by boiling silver oxide with potassium ferricyanide, on continuing the ebullition ammonia is evolved and the precipitate becomes black. The filtrate from the pink precipitate contains potassium cyanide and silver ferrocyanide in large quantities, and small quantities of silver cyanide and potassium formate. The final black precipitate consists of metallic silver and ferric oxide; the filtrate from it contains the same constituents as the pink precipitate filtrate, with the exception that there is no potassium formate, but instead silver ferricyanide. When ammoniacal solutions of silver cyanide and silver ferricyanide are boiled together, a buff precipitate is produced, which behaves like the above-mentioned pink precipitate (thus synthesising the compound of silver cyanide with silver ferricyanide). The potassium cyanide then reduces the remaining silver ferricyanide to ferrocyanide thus:  $2\text{Ag}_6\text{Fe}_2\text{Cy}_{12} + 4\text{KCN} + 4\text{H}_2\text{O} = 3\text{Ag}_4\text{FeCy}_6 + \text{K}_4\text{FeCy}_6 + 2\text{HCN} + 2\text{CO}_2 + 2\text{NH}_3$ . When silver oxide and silver ferrocyanide are boiled together, the pink precipitate, silver cyanide, and ferric oxide are produced:  $\text{Ag}_6\text{Fe}_2\text{Cy}_{12} + 3\text{Ag}_2\text{O} = 12\text{AgCy} + \text{Fe}_2\text{O}_3$ . Several equations are given to illustrate the reactions which probably take place during these changes.

D. A. L.

**Test for Gallic Acid.** By S. YOUNG (*Chem. News*, 48, 31–32).—When aqueous gallic acid is treated with potassium cyanide solution, a red coloration is produced, which disappears in a short time if the liquid remains undisturbed. If, however, the liquid is shaken energetically the colour reappears, but again disappears on standing. The

colour can be reproduced in this manner from 15 to 20 times, the solution finally becoming brownish-yellow. Pure tannic acid, free from gallic, is not coloured by potassium cyanide. D. A. L.

**Examination of Fatty Almond Oil.** By H. HAGER (*Dingl. polyt. J.*, 248, 524).—The author draws attention to the fact that the oil obtained from bitter almonds differs from that of sweet almonds by the elaidin test, as it gives only a small amount of solid elaidin. For the examination of the oil, 1 gram is treated in a small porcelain dish with 4 drops of concentrated sulphuric acid, and the mixture stirred together with a glass rod. A yellow colour rapidly changing to yellow-red appears, which is soon converted into a permanent brown with green tinge, or green with brown tinge. By mixing equal volumes of fuming nitric acid and water with 7 vols. of almond oil, and agitating the mixture, the oil from sweet almonds gives a white colour, whilst that from bitter almonds yields light to dark-yellow shades. D. B.

**Butter Analysis.** By A. v. BASTELAER (*Bied. Centr.*, 1883, 419).—In order to determine the relations of water, fat, casein, and salt, the author takes 10 grams from the centre of a butter sample, places it in a porcelain dish of 5 or 6 cm. diameter; dried at 100—120° to constant weight, the loss is water; the residue is extracted with rectified benzene, the first portion poured on without stirring to allow the casein to separate, the last two portions stirred up with a glass rod, and again dried; the loss shows fat; residue ignited is casein by loss; the ash is salt. The limits of a large number of determinations are given:—

Pure butter fat. ....	75 to 85 per cent.
Water .....	9 to 15    "
Casein .....	1 to 3     "
Sodium chloride ....	5 to 10    "

J. F.

**Tests for Vegetable Alkaloids.** By R. PALM (*Chem. News*, 48, 65—66).—The author has shown previously that the alkaloids are precipitated by solutions of alkaline sulphides or persulphides, and moreover that in contact with a solution of sodium thioantimonate, solutions of the alkaloid salts form characteristically coloured precipitates consisting of the alkaloid hydrosulphides mixed with antimony sulphide. When the solutions of the alkaloid and reagent are dilute, these precipitates appear as colourless turbidities, which become yellow on exposure to the air; whilst with concentrated solutions they are yellow to reddish-brown, and in saturated solutions they form resinous masses. The precipitation is more complete in dilute solutions, and is accelerated by gently heating, or by the addition of strong alcohol. In most cases the yellow precipitates are dissolved by excess of the thioantimonate; they are, with few exceptions, amorphous, and dilute acids only partially separate the alkaloid from them. The chemical composition of the precipitates has not been determined. Sodium thioantimonate produces the following changes



with the alkaloids referred to. With quinine sulphate in dilute neutral solutions, a white turbidity; in stronger solutions, yellow flocks, which on shaking form resinous lumps, and become darker. When hot solutions of the quinine salt and reagent are mixed, resinous masses form at once, which when dry fall to a fine yellow powder like lead iodide. With cinchonine sulphate, in dilute solutions, dark yellow (leather colour) flocks form at once; they do not coagulate either on standing or heating. With quinidine sulphate, the effect is almost exactly the same as with the quinine salt, with the exception that the whole of the precipitate does not become resinous, and when dry is of a darker yellow colour (an intense dark chrome-yellow): the precipitation is also more complete. With morphine hydrochloride in dilute solutions, yellow flocks are at once deposited, which are darker in strong solutions, and when dry resemble powdered gamboge in colour. With codeine hydrochloride, a flocculent precipitate is produced, which when dry resembles the quinidine precipitate in tone, being a paler yellow than the morphine precipitate. With narcotine, in concentrated hot solutions, the precipitate coagulates in resinous masses, which when dry have the colour of dry precipitated ferric hydroxide. With strychnine nitrate, the reaction is more sensitive than with all the other vegetable alkaloids, the strychnine being entirely precipitated, and moreover the precipitate is not soluble in excess of the reagent. In dilute solutions of strychnine nitrate, colourless flocks separate which become yellowish in air; in concentrated solutions, yellow flocks form which do not coagulate on standing, and when dry are of a fine intense deep golden-yellow colour. With brucine nitrate, when the reagent is added in successive portions to a moderately concentrated solution of this alkaloid salt, three distinct precipitates are obtained: 1. Reddish-yellow, which collects in resinous masses. 2. Light golden-yellow flocks. 3. Colourless flocks, which form a crust on the surface of the liquid. When the mixed precipitates are boiled with water, the greater part dissolves, leaving an amorphous deep orange residue. The solution deposits yellow crystals of the double sulphide.

With atropine sulphate in strong solutions, a yellow deposit is formed, which coagulates on shaking or heating, but when dry is not so dark as the dry morphine precipitate.

With bebeerine hydrochloride, a dark-coloured precipitate is formed which coagulates in strong, and especially in hot, solutions, and when dry is greyish-brown. The alkaloids also form double sulphides with other metallic sulphides.

Lead chloride can be used as a reagent for vegetable alkaloids; it should be dissolved in a solution of sodium chloride, which dissolves more of the lead salt than cold water does. The precipitates are generally crystalline, and consist of a mixture of lead chloride and an alkaloid salt. Quinine and brucine form crystalline powders; cinchonine, morphine, and codeine small fine needles; the strychnine precipitate when dry forms a crystalline asbestos-like felted mass. The lead chloride is not so delicate a test as the thioantimonate. A strong solution of sodium chloride completely precipitates bebeerine from its solutions.

D. A. L.

**Estimation of Urea.** By L. HUGOUNENQ (*Compt. rend.*, **97**, 48—49).—Urine is filtered through animal charcoal, diluted with water, and heated in sealed tubes at a temperature above  $140^{\circ}$ , the ammonium carbonate which is formed being estimated by means of standard acid with "methyl orange" as indicator. This method is applicable to albuminous urine, if the albumin is previously removed by coagulation, but it is not applicable to urine containing glucose or a notable quantity of magnesium. C. H. B.

**Estimation of Gluten in Flour.** By L. REED (*Chem. News*, **48**, 63).—The proposed method of estimation is based on the fact that a yellow nitro-body is produced by the action of nitric acid on albuminoids.

Half a gram of flour is put in a test tube, which is graduated from the bottom to about half way up into 4 parts of equal capacity, water is added up to the 4th mark, and the tube violently shaken. The contents are now temporarily transferred to a dry tube, the graduated tube is washed, and a quarter of the liquid poured back up to 1st mark, and colourless nitric acid is added up to 3rd mark. After five minutes' standing, with occasional shaking, the liquid is filtered through a dry filter into a dry receptacle; a standard flour is treated in the same way, and the clear yellow solutions are examined colorimetrically, the qualities of the flours being inversely as the heights of equal colour. D. A. L.

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## Technical Chemistry.

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**Heat of Combustion of Coal.** By SCHEURER-KESTNER (*Compt. rend.*, **97**, 268—271).—A criticism of Bunte and Stohmann's experiments (Munich, 1879, 1880, 1882). C. H. B.

**Influence of Artificial Lighting on the Atmosphere of Dwellings.** By F. FISCHER (*Dingl. polyt. J.*, **248**, 375—379).—The author shows that the preference given to solar oil or rock oil as illuminating agents is not only based on grounds of economy, but depends on the fact that these oils contaminate the air of rooms less largely than coal-gas. Gas is, however, a more convenient and effective illuminant. The use of regenerative gas-burners, or of the electric light especially in the form of incandescent lamps worked from accumulators, is strongly recommended, as little or no heat is given off, whilst the atmosphere is not contaminated with injurious substances. D. B.

**Chemical Composition of the Water of the Danube above Vienna in the year 1878.** By J. F. WOLFBAUER (*Monatsh. Chem.*, **4**, 417—435).—This paper gives the results of a series of analyses of Danube water made in the year 1878, chiefly with the view of ascer-

taining the value of the water for irrigating a tract of land known as the Marchfeld, situated between the rivers Danube and March. For this purpose 23 samples of water were taken at Grafenstein, about 20 kilometers above Vienna, at intervals of 16 days from January 20, 1878, to January 16, 1879, the height of the river being observed at each taking. The quantities of solid constituents of the water in the forms of dissolved and of suspended matter (mud) were then determined in each sample, and the several samples were submitted to chemical analysis. The results are given in the following table,

TABLE I.—*Average Chemical Composition and Hardness of Danube Water in Four Periods of the Year 1878.*

10,000 parts by weight of turbid water contain :	In the periods :				
	I.	II.	III.	IV.	
	including the samples from				
	Jan. 1	May 7	Sept. 10	Nov. 9	
	to				
	May 2	Aug. 26	Oct. 23	Jan. 16	
Parts by weight.					
Suspended matter (mud)					
Total amount .....	1·219	1·654	0·765	0·148	
Including: organic matter and chemically combined water (loss by ignition).....	0·079	0·072	0·021	0·003	
Carbonates, &c. ....	0·510	0·766	0·355	0·072	
Sand and clay.....	0·630	0·816	0·389	0·073	
Dissolved non-volatile substances: total directly determined .....	1·727	1·461	1·781	1·952	Annual average
Organic matter .....	0·070	0·042	0·052	0·059	0·056
Silica.....	0·054	0·039	0·048	0·052	0·048
Ferrous oxide .....	0·004	0·005	0·002	0·002	0·003
Lime.....	0·608	0·543	0·643	0·710	0·616
Magnesia.....	0·176	0·128	0·175	0·199	0·166
Soda .....	0·049	0·028	0·036	0·040	0·038
Potash.....	0·017	0·016	0·024	0·020	0·019
Chlorine .....	0·034	0·016	0·018	0·024	0·024
Sulphuric anhydride .....	0·118	0·106	0·123	0·154	0·123
Nitric anhydride.....	0·020	0·013	0·013	0·024	0·018
Carbonic anhydride (combined) ..	0·621	0·524	0·652	0·706	0·615
Total.....	1·771	1·460	1·786	1·990	1·726
Deducting oxygen equivalent to chlorine .....	0·008	0·004	0·004	0·005	0·005
there remains for calculated sum of dissolved fixed substances....	1·763	1·456	1·782	1·985	1·721

TABLE I (*continued*).

or combining the Acids and Bases :—

10,000 parts by weight of turbid water contain :	In the periods :				Annual average.
	I.	II.	III.	IV.	
	including the samples from				
	Jan. 1	May 7	Sept. 10	Nov. 9	
	to				
	May 2	Aug. 26	Oct. 23	Jan. 16	
Parts by weight.					
Calcium carbonate .....	0·969	0·864	1·041	1·105	0·979
Magnesium carbonate .....	0·370	0·269	0·368	0·418	0·349
Ferrous carbonate .....	0·006	0·008	0·003	0·003	0·005
Calcium sulphate .....	0·158	0·143	0·146	0·229	0·165
Potassium sulphate .....	0·031	0·030	0·044	0·037	0·034
Sodium sulphate.....	0·018	0·015	0·029	0·012	0·018
Sodium nitrate .....	0·031	0·020	0·021	0·037	0·028
Sodium chloride.....	0·056	0·026	0·030	0·040	0·039
Silica .....	0·054	0·039	0·048	0·052	0·048
Organic matter .....	0·070	0·042	0·052	0·059	0·056
Total.....	1·763	1·456	1·782	1·985	1·721
In Fehling's degrees.					
Hardness {	permanent .....	5·5	4·6	4·6	5·4
	temporary .....	4·6	4·5	6·0	6·2
	total .....	10·1	9·1	10·6	11·6

which shows the average composition of the Danube water in four seasons of the year 1878, together with the average for the whole year; also the degrees of hardness according to Fehling's scale, in which 1° of hardness indicates the presence of 1 part by weight of calcium oxide in 100,000 parts of water.

The numbers in Table I show that the minima of dissolved substances and of hardness occur in the spring and early summer months, when the river is swollen by rainfalls and by the melting of the Alpine snows. The variations in the proportion of mud at different seasons are much greater than those of dissolved matters, the minimum 0·96 per cent. being observed on the 11th of December, and the maximum 3·383 on the 6th of July. The water is clearest from the beginning of October to the middle of January, from which time till the beginning of autumn incessant fluctuations take place in the height

of the river, and in the quantity of mud which it carries along. The general result of all these observations is that as the river rises, it becomes more muddy and softer, and as it sinks, it becomes clearer and harder.

TABLE II.—*Average Quantity and Composition of the Mud.*

10,000 parts of turbid water contain suspended as mud :	In form of :				Total.
	Organic matter and chem. comb. water (loss by ignition).	Carbonates, soluble silicates, &c., soluble in nitric acid.	Argil- laceous sub- stance, dis- integrable by strong sulphuric acid.	Sand.	
	Parts by weight.				
	0·050	0·4658	0·1857	0·3362	
Composed of :					
Ferric oxide.....	—	0·0253	0·0197	0·0031	0·0481
Alumina .....	—	0·0348	0·0433	0·0328	0·1119
Lime.....	—	0·1505	0·0031	0·0006	0·1542
Magnesia .....	—	0·0561	0·0053	0·0019	0·0633
Soda .....	—	0·0029	0·0020	0·0080	0·0129
Potash .....	—	0·0037	0·0093	0·0045	0·0175
Carbonic anhydride ..	—	0·1720	—	—	0·1720
Phosphoric „ ..	—	0·0017	—	—	0·0017
Silica .....	—	0·0188	0·1020	0·2853	0·4061

The preceding data afford the means of estimating the quantities of mud and of plant-constituents which the water of the Danube is capable of yielding for irrigation. According to the proposed scheme for irrigating the Marchfeld, 1·2 litre of water per second would be made to flow over each hectare of surface, during the normal irrigation period, from April to September inclusive.

This amounts to 18,000 kilos. per hectare, or, in other words, the depth of the layer of water added daily to the soil would amount to 10 mm. With this quantity of water there would be added to the soil—

Floating particles (mud) .....	2500 kilos.
Dissolved matter (total) .....	2800
Potash, dissolved .....	31 kilos.
„ in the form of zeolitic silicates	62
and clay .....	
Phosphoric acid .....	4·1
Sodium nitrate.....	46·0

For the better appreciation of these numbers, it may be added that

the quantity of potash thus added to the soil might be estimated to increase the production of hay by 4000 kilos. per hectare. The phosphoric acid in the water may be roughly estimated as equivalent to the production of 970 kilos. per hectare. H. W.

**Organisms in the Air around Carlsberg.** By E. C. HANSEN (*Bied. Centr.*, 1883, 279—283).—By employing sterilised hopped beer-wort the author has examined the air in various localities at Carlsberg, including the fermenting cellars of a brewery. He gives a long list of the various organisms found, and states that all the organisms found in different parts of the brewery were also found in a garden, excepting *Sacch. glutinis* and *sarcina*, *Ba. spirilla* and *spirochetis* were never found. Grains should not remain in a brewery, as bacteria proceed from them, which may set up acid fermentation. Alcohol ferments proceed from ripe fruits and the soil, and of these ferments mildew is the most abundant and saccharomyces the least frequent. E. W. P.

**Coking of Coal with Conversion of its Nitrogen into Ammonia.** By SCHEURER-KESTNER (*Comp. rend.*, 97, 179—182).—The loss of heat-producing power resulting from the preliminary coking of coal is only compensated by the value of the condensed ammonia compounds when the price of the original coal is extremely low. C. H. B.

**Manufacture of Sulphuric Acid free from Arsenic and Selenium.** By H. BORNTÄGER (*Dingl. polyt. J.*, 248, 380).—With the view to facilitate the drying and roasting operations, the author recommends to filter-press the iron sulphide formed in the manufacture of sulphuric acid from the soda residues of the Leblanc process by the aid of spent pyrites (*ibid.*, 243, 151) instead of draining it on filters. It is also suggested to utilise the resulting liquors for the preparation of sodium thiosulphate, as they are free from metallic sulphides. D. B.

**Manufacture of Sulphuric Acid.** By H. PEMBERTON (*Dingl. polyt. J.*, 248, 424).—The author has experimented on the manufacture of sulphuric acid from sulphur, with the view of determining the relation between the consumption of nitre and the chamber-space. His results are of interest, as they include a system which works with Gay-Lussac towers. From the amount of denitrated Gay-Lussac acid, the quantity of nitre which passed through the chambers for 100 parts of sulphur is calculated. The percentage of nitre consumption found is 15.6, which includes 3.5 per cent. of nitre lost.

Hurter, in his dynamic theory of the manufacture of sulphuric acid, found that the product of chamber-space into nitre consumption is approximately a constant number when the chamber-space corresponds to 1 per cent. of loss of nitre for works not using Gay-Lussac towers. The chamber-space is inversely proportional to the nitrogen compounds present, provided, however, that the loss of sulphur is the

same, and the same strength of acid is made. For works making weak acid the necessary chamber-space is much smaller.

The following results by Hurter are yearly averages of five English works using pyrites. The author's numbers refer to works where sulphur is exclusively used. The two are not, however, comparative, as in the author's case the loss of sulphur and the concentration of the acid is not shown :—

*Hurter's Results (only Pyrites).*

	Chamber space for 1 pound of sulphur. cubic feet.	Nitre used for 100 sulphur.	Product of nitre, consumption into chamber space.	Acid produced from 100 sulphur.	Sp. gr. of acid.
A ....	32·3	10·0	323	431	1·55
B ....	29·8	11·2	334	392	1·65
C ....	24·5	12·0	294	345	1·65
D ....	22·3	13·7	305	386	1·65
E ....	22·8	9·5	217	405	1·50

*Pemberton's Results (Sulphur).*

1....	26·8	10·0	268	—	—
2....	29·8	9·0	268	—	—
3....	35·7	8·0	285	—	—
4....	19·2	15·6	300	—	—

In the case of A and E the acid is much weaker; the produce from A is larger, and the chamber-space in the case of E much smaller. No. 4 was worked with Gay-Lussac towers, the loss of nitre being 3·5 per cent. D. B.

**Formation of Sodium Sulphate in Bricks.** By G. CHRISTEL (*Arch. Pharm.* [3], 21, 39—41).—The author found that a mass of effloresced salt, which appeared upon some bricks in cold weather, consisted of sodium sulphate with a trace of sodium carbonate. The principal chemical constituents of the materials used in the manufacture of the bricks were aluminium silicate, iron pyrites, and sodium silicate. The author supposes that the formation of sodium sulphate may be due to one or all of the following reactions :—(1.) The iron pyrites, under the influence of heat in presence of water, absorbed oxygen, forming iron sulphate and sulphuric acid; the latter acting on sodium silicate would form sodium sulphate; the sulphuric acid formed in the above manner would also act on aluminium silicate, giving rise to sodium alum, which, when heated, would yield alumina and sodium sulphate. (3.) The existence of calcium sulphate or other sulphate in the original materials, which, during manufacture, would act on a sodium salt yielding sodium sulphate by double decomposition. W. R. D.

**New Process for Producing a Bronze-coloured Surface on Iron.** By L. MAYER (*Dingl. polyt. J.*, 248, 249).—The cleaned objects are exposed to the vapours of a heated mixture of concentrated



hydrochloric and nitric acid (1 : 1) for a few minutes, and heated to a temperature of 300—350°, the heating being continued until the bronze colour appears. The objects are then cooled, rubbed with vaseline, and heated, until the latter begins to decompose. This operation is then repeated. A bronzy oxide coating is obtained by using acetic acid in conjunction with the above-mentioned acids. By varying the proportions of the different acids, it is possible to obtain light or dark brown shades. The author has coated iron T-bars in this manner and exposed them for about a year to the atmosphere of his laboratory without the slightest change or sign of corrosion.

D. B.

#### **Production of a Gold-coloured or Green Surface on Brass.**

By C. PUSCHER (*Dingl. polyt. J.*, 248, 304).—40 grams of caustic soda, 40 of milk-sugar, and 1 litre of water, are boiled together for 15 minutes. 40 grams of a cold saturated solution of sulphate of copper are then added gradually, the mixture being stirred continually. The solution is then cooled to 75°. A short immersion of the articles to be coated results in the formation of a gold colour. A longer digestion yields a bluish-green tint, whilst after a very long immersion iridescent colours are obtained.

D. B.

#### **Adulteration of Cement.** (*Dingl. polyt. J.*, 248, 245—249).—

At the sixth general meeting of the Society of German Cement Manufacturers, held in Berlin, a long discussion on the adulteration of Portland cement took place, and the following propositions were unanimously agreed to:—

(1.) Portland cement is a product formed by intimately mixing lime and alumina, burning the mixture to the point at which the mass begins to slag, and disintegrating it to the fineness of flour.

(2.) Every product which is formed in a different manner or receives foreign additions during or after burning, is not to be regarded as Portland cement. Additions of 2 per cent. of gypsum are, however, admissible.

(3.) The sale of cement containing foreign substances as Portland cement is an imposition on the consumers.

(4.) Good Portland cement is not improved by mixing foreign substances like calcium silicate (ground blast-furnace slag) trass, ground clay, slate, limestone, &c., with it. But supposing it could be shown that such additions were of advantage, they should not be allowed, as the consumer cannot control the quantity or quality sufficiently to enable him to guard himself against fraud.

(5.) Every addition is therefore to be regarded as the commencement of the preparation of mortar, and concerns, not the manufacturer, but the consumer.

(6.) As the test which is used at the present time is unavailable when Portland cement is adulterated with foreign substances, and the character of cement is altered when such additions are made, it is useless to apply the same in comparing mixed with unmixed cement.

D. B.

**Metallurgy of Nickel.** By W. P. BLAKE (*Chem. News*, **48**, 87—89).—In an interesting address, the author remarks that for many years after its discovery nickel was produced only as a bye-product in the working of cobalt ores, and even when it came into use, it appeared only as an alloy, and until 1876, when Wharton in America investigated the subject and produced considerable quantities of the metal, pure nickel was as rare as thallium is at the present time. Subsequently Fleitman improved and cheapened the refining operations, and reduced the liability to the presence of blow-holes in nickel castings, by adding a very small quantity of magnesium to the molten metal in the pot. By this means the carbonic anhydride is destroyed, magnesia and graphite being formed. Since then large quantities of the pure metal have been produced, and many uses found for it. Nickel welds well with iron, and the two metals when rolled together at the proper temperature, become so firmly united that they may be rolled down together to any thinness. There are all thicknesses of nickel upon iron.

In scrap or waste, the nickel is recovered by dissolving away the iron with sulphuric acid. Formerly nickel plates, &c., were beaten directly under the hammer: hence there was a great loss by scaling, as with iron, but now this is avoided by covering the nickel with a thin sheet of iron, which is afterwards dissolved off. This nickelled iron is extremely useful; the coating is much more firmly attached, and hence more durable than the electrically deposited nickel, whilst for domestic purposes, for covers, saucepans, &c., it surpasses *tinned* iron or copper, for the nickel is not only lighter, harder, and stronger, but is also less liable to tarnish and corrode, so that it can always be kept polished. It moreover will wear longer, and cannot be melted off by overheating.

D. A. L.

**Novelties in the Iron Industry.** (*Dingl. polyt. J.*, **248**, 498—509.)—In a paper read at the August meeting of Mechanical Engineers, Cochrane referred to the working of blast furnaces, and especially to the effect which the position of the tuyeres has on the working of the furnace. The position of the tuyeres if badly chosen may often annul the saving effected by working with large furnaces and a specially hot blast. By drawing back the tuyeres a great advantage is gained; thus by increasing the distance of the tuyeres from 1.83 meters to 2.13 the make of iron was raised from an average of 483 tons to 599 tons, the consumption of coke being practically the same in both cases (603 tons).

According to Delafond, the dephosphorisation of pig-iron in basic lined open hearths has the following advantages over the converter. The preparation and maintenance of the basic lining is not attended with the same difficulties. The addition of lime and the removal of slag can be effected at any period of the operation.

Gautier states that the pressing of fluid steel during the process of cooling is conducted at the Whitworth Steel Works by pouring the fluid metal into moulds composed of a series of superposed steel rings lined with a refractory material. The moulds are placed on wheels, and when full are run under the hydraulic presses. A refractory

stone prevents the ram of the press from being welded together with the steel. The pressure used is equal to 600 atmospheres. Steel prepared by compression is said to gain considerably in hardness.

The longer the surface of a casting is allowed to remain in the fluid state, the more uniformly will it contract on cooling, and the smaller will be the number of hollow spaces which are formed. Krupp has utilised this circumstance in practice by surrounding the upper sides of the castings with fluid slag or sand.

Gmelin recommends the use of a jacketted cylinder cooled by water for the walls of cupolas.

Dufrené has patented a new arrangement in cupolas heated by gas, the generator being in direct communication with the furnace. In the lower part of the collecting space immediately above the opening through which the fire gases enter, an intermediate hearth is arranged, consisting of a series of barrelled ribs, so as to allow the flame to pass into the charge which is placed on the hearth.

Besson has modified the construction of cupolas by connecting the chamber of the furnace with a separate iron hearth and a special combustion space, which is said to accelerate the fusion.

Reusch works up scrap iron by heating it to redness in a furnace with a reducing flame, whereupon it is pressed into moulds and rolled out to bars, plates, &c.

D. B.

**Red Wine Manufacture in Germany.** By NESSLER (*Bied. Centr.*, 1883, 422—423).—The growth of a taste for red wines in Germany, and the planting of new vineyards to supply it in the vine districts, has induced the author to publish the recommendations contained in the present paper. They relate to situation of the vineyard, and the descriptions of grapes which should be grown; he discusses the kind of vats which should be used, and recommends a large chamber or other place which can be kept at a uniform temperature of 16—20°, in which the process of fermentation should be carried on independent of outside temperature: he cautions the wine maker against the use of unripe or spoiled grapes.

J. F.

**Extractive Matter in Tyrolese Wine, 1883 Vintage.** By A. HENECKE (*Bied. Centr.*, 1883, 426).—It is the custom to examine the yearly averages of wines grown in the district; as those of 1882 were of inferior quality to those of many previous years, it was expected that the extractive matter would have been very low. The reverse was the case, however, and the author endeavours to explain this by supposing that in plentiful years the poor and spoiled bunches are left, the superior chosen for wine making. During the year in question, there were few choice bunches, and the decayed or unripe grapes yielded a large extract. The wine of the year was thick and mucilaginous, cleared badly, and developed bacteria in quantity. He attributes it to the low proportion of alcohol in the wine.

J. F.

**Preservation of Wines.** By E. HOUDART (*Compt. rend.*, 97, 55). The second fermentation of light wines rich in sugar, such as the "vins de coupage," when kept in casks for daily consumption, may be prevented by carefully heating the wine to 55—60° in a specially constructed apparatus, and storing it in casks previously well washed

with boiling water. The air which enters the cask when the wine is drawn off, is filtered through cotton-wool. This treatment does not appreciably affect the composition, colour, flavour, nor any other property of the wine.

C. H. B.

**Wine and its Examination.** (*Dingl. polyt. J.*, 248, 293—296.)

According to Maumené, cenocyanin, the colouring matter of wine, is colourless at the commencement of the ripening of grapes, and is rendered blue by oxidation; iron takes no part in this change.

For the preparation of wine from roots, Brin recommends the following method. Beetroots are boiled, triturated and pressed; the juice is brought into fermenting vats provided with steam pipes and fermented with yeast, malt, or apple-juice. The requisite quantity of tannic acid is then added, the mixture allowed to settle, filtered, and the product treated like ordinary grape-wine. This product is said to form a suitable adulterant for red wines. Turnips yield a white coloured wine when treated in a similar manner; it is, however, advisable to add a small quantity of nitric acid to the mass at the beginning of the fermentation.

*Lorraine Wines.*—Weigelt has prepared a number of wines from grapes of the year 1881, and examined the same with the following results:—

	Mörching.	Hayingen.	Novéant.	Corny.	St. Julien, near Metz.*
Alcohol per cent. by weight..	6·210	6·280	6·570	7·000	7·270
Extract .....	2·118	2·067	2·000	2·078	1·981
Non-volatile acid .....	0·420	0·420	0·495	0·528	0·495
Volatile acid .....	0·195	0·117	0·117	0·157	0·170
Free tartaric acid .....	0·026	0·015	0·023	0·028	0·034
Glycerol .....	0·638	0·503	0·403	0·244	0·529
Mineral substances .....	0·168	0·169	0·156	0·190	0·176
Sulphuric anhydride .....	0·006	0·008	0·004	0·004	0·006
Phosphoric anhydride .....	0·024	0·035	0·026	0·028	0·030
Polarisation .....	±0	−0·1	±0	±0	+0·1

	Ars on the Moselle.	Wallières.	Marsal.	Barzel- lona.	
Alcohol per cent. by weight..	7·470	7·930	10·460	12·000	
Extract .....	2·264	2·787	2·261	2·528	
Non-volatile acid .....	0·480	0·480	0·907	0·412	
Volatile acid .....	0·155	0·202	0·135	0·187	
Free tartaric acid .....	0·029	0·033	0·041	0·059	
Glycerol .....	0·439	0·380	—	0·773	
Mineral substances .....	0·206	0·255	0·155	0·205	
Sulphuric anhydride .....	0·009	0·007	0·004	0·126	
Phosphoric anhydride .....	0·047	0·033	0·036	0·031	
Polarisation .....	−0·2	−0·1	+0·2	−0·2	

\* Red and white grapes.

Fresenius and Borgmann (*Zeitschr. Anal. Chem.*, 1883, 46) give a description of their investigation on pure grape wines.

Borgmann confirms the assumption that wine which contains less than 7 pts. glycerol for 100 pts. alcohol, has been treated with alcohol.

D. B.

**Preparation of Spirit and Pressed Yeast.** (*Dingl. polyt. J.*, 248, 464—469.)—At the annual meeting of the Society of German Spirit Manufacturers, the more recent experience gained in the manufacture of spirit and pressed yeast was discussed.

Delbrück treated of the improvements which have been effected in the manufacture of spirit by the introduction of new mashing apparatus. Referring to the preliminary mashing vats used for mixing the malt and the stuff coming from the steamers, both of which are introduced at different temperatures, it is stated that the main object is to obtain perfect agitation, so that no differences of temperature can be noticed at any period of the mashing. With regard to the mode of cooling, a very advantageous arrangement is the use of an exhauster, although cooling by means of water is more trustworthy.

According to Märker, Goutart's mashing apparatus is the most perfect in mechanical construction and working power; a very concentrated mash is obtained by its use.

Francke discussed in detail the conditions necessary to produce the highest yield of yeast.

D. B.

**Bread Making.** By V. MARCANO (*Compt. rend.*, 96, 1733—1734).—In experiments on bread-making made in Venezuela, the author found that the fermenting paste is free from *saccharomyces*, but contains a large number of moving spherobacteria. During fermentation, the gluten and a small portion of the albuminoids are partially dissolved and converted into peptones not precipitable by tannin. These results agree with those of Chicandard (*Abstr.*, 1883, 1179), but the author found that contrary to the statement of this chemist, the paste at the commencement of fermentation contained a considerable proportion of erythro-dextrins and a relatively small quantity of soluble starch, whilst at a later stage it also contained a notable proportion of achroo-dextrins. In Venezuela, the bread is made from a mixture of flour and starch which is comparatively poor in gluten. The bacterium does not attack the starch until after it has destroyed the albuminoids, hence the necessity for using a very active ferment developed by means of maize, potatoes, &c. Similar fermentation takes place whenever any grain, fruit, root, &c., is exposed to the air in the tropics. If European yeast is placed in moistened starch, the yeast gradually disappears, and is replaced by bacteria. Attempts to repeat these experiments in Paris have yielded negative results, the starch always remaining unattacked. It would appear, therefore, that in all experiments on fermentation, it is necessary to take into account the local conditions, which may exert great influence on the nature and progress of the change.

C. H. B.

**Fermentation of Bread.** By L. BOUTROUX (*Compt. rend.*, 97, 116—119).—Leaven from rye-bread made at a farm at a considerable

distance from a brewery was found to contain bacteria and four other distinct organisms, viz., *Mycoderma vini*, two distinct species of yeast different from that of beer and wine, and an organism which appears to be *Saccharomyces minor*, but which has no power as a ferment. The bacteria were very abundant, but the other organisms could only be recognised by careful cultivation, and it would appear therefore that the bacteria are the principal agents of fermentation, the other organisms playing a secondary and comparatively insignificant part.

C. H. B.

**Percentage of Sugar in Beet.** By K. STAMMER and P. DEGENER (*Bied. Centr.*, 1883, 274—278).—Stammer has introduced a pulper which enables a higher percentage of sugar to be obtained in the manufacture of beet-sugar, and he shows the gain obtained by successive pressings of the pulp. Beets which have gone to seed and others which have withered, are by no means wanting in sugar. After the mash has been extracted with 50 per cent. alcohol, it still yields sugar to 75 per cent. alcohol. Degener describes his method for estimating the value of roots, which method yields higher results than that of Scheibler, as modified by Seckel.

E. W. P.

**Strontia Process.** By C. SCHEIBLER (*Dingl. polyt. J.*, 248, 426—428).—The author mixes a 20 to 25 per cent. solution of pure cane-sugar heated to 70° to 75° with strontium hydroxide in the proportion of 1 mol. sugar to 1 mol.  $\text{SrH}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ , stirring the liquor continually. On cooling, a supersaturated solution of strontium monosaccharate is obtained, from which, after some time, either unaltered strontium hydroxide crystallises out or monosaccharate separates according as the saturated solution has been treated with a few crystals of strontium hydroxide, or a small amount of monosaccharate. The saccharate,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{SrO} \cdot 5\text{H}_2\text{O}$ , is formed in the cold by introducing the requisite quantity of finely-divided strontium hydroxide into a cold sugar solution, with constant agitation. The author utilises this reaction for the recovery of sugar from molasses. He dissolves 0.5 k. of strontium hydroxide in 1.5 k. of boiling water, and mixes it with 1 k. molasses. The clear solution is allowed to cool and stirred frequently, small quantities of monosaccharate being added at the same time. After 12 to 24 hours, the strontium saccharate has crystallised out; it is freed from the mother-liquor by filter presses, and washed with water or a cold saturated solution of strontium hydroxide. In order to recover the sugar which remains in the liquors, an excess of strontium hydroxide is added, and the mixture boiled for some time: thus nearly all the sugar is precipitated as strontium disaccharate; the strontium hydroxide remaining in solution is precipitated with carbonic anhydride. The disaccharate which is saturated with mother-liquor is converted into monosaccharate by dissolving it in molasses and adding a hot saturated solution of strontium hydroxide (1 mol. total sugar requires 1.25 mols. strontium hydroxide). The strontium monosaccharate is separated in the manner just described. From the latter, the sugar is recovered by the ordinary methods, or the strontium hydroxide may be first partly separated as such and again used for a further operation. For this

purpose the saccharate is dissolved in hot, but not boiling water, and the solution allowed to cool without agitating it, when strontium hydroxide crystallises out.

The author has determined the solubility of strontium monosaccharate in water at different temperatures. The following table gives the solubilities to 60°, the temperature at which the decomposition of the saccharate commences :—

Temperature.	One litre contains—				Sp. gr. of the monosaccharate solution at +17·5°.	Corresponds with degrees, Brix.
	Monosaccharate, $C_{12}H_{22}O_{11}SrO$ .	Sugar.	Strontium oxide, $SrO$ .	Crystalline strontium hydroxide, $H_2SrO_2 \cdot 8H_2O$ .		
	grms.	grms.	grms.	grms.		
0	28·4	21·80	6·60	16·93	1·01775	4·51
2	30·2	23·18	7·02	18·00	1·01892	4·81
4	32·0	24·56	7·44	19·07	1·02000	5·08
6	33·9	26·03	7·87	20·21	1·02119	5·37
8	35·7	27·41	8·29	21·28	1·02231	5·65
10	37·5	28·79	8·71	22·35	1·02344	5·93
12	39·5	30·32	9·18	23·54	1·02469	6·24
14	41·6	31·93	9·67	24·79	1·02600	6·56
16	43·8	33·62	10·18	26·10	1·02738	6·90
18	46·2	35·46	10·74	27·53	1·02888	7·27
20	48·6	37·31	11·29	28·96	1·03038	7·64
22	51·2	39·31	11·89	30·51	1·03200	8·03
24	53·9	41·38	12·52	32·12	1·03369	8·44
26	56·7	43·53	13·17	33·79	1·03544	8·87
28	59·7	45·83	13·87	35·58	1·03731	9·32
30	62·7	48·13	14·57	37·37	1·03919	9·77
32	65·8	50·51	15·29	39·21	1·04113	10·24
34	69·3	53·20	16·10	41·30	1·04331	10·76
36	73·2	56·18	17·02	43·62	1·04575	11·34
38	77·5	59·49	18·01	46·19	1·04844	11·98
40	82·3	63·18	19·12	49·05	1·05144	12·69
42	87·8	67·40	20·40	52·33	1·05488	13·50
44	93·8	72·01	21·79	55·90	1·05863	14·37
46	100·7	77·31	23·39	60·01	1·06294	15·37
48	109·7	84·21	25·49	65·38	1·06856	16·67
50	121·9	93·58	28·32	72·65	1·07619	18·40
52	124·3	103·10	31·20	80·04	1·08394	20·14
54	147·0	112·85	34·15	87·61	1·09188	21·91
56	162·9	125·05	37·85	97·08	1·10181	24·08
58	185·1	142·10	43·00	110·31	1·11569	27·06

D. B.

### Preparation of Potato Starch. (*Dingl. polyt. J.*, 248, 381.)—

Nitykowski has made a series of comparative tests on the cultivation of potatoes. He found that the recent heavy rains have reduced the total yield of potatoes by about 25 per cent. of the average of the last ten years. Thirty-seven varieties were examined, the yield ranging from 9697 kilos. per 5000 square meters (containing 19·16

per cent. starch, equal to 1858 kilos.) to 4167 kilos. (containing 16·38 per cent. starch, equal to 683 kilos. starch per 5000 square meters). The so-called "alcohol potatoes" proved to be the most mealy and richly flavoured. The yield was 7500 kilos. per 5000 square meters (containing 19·26 per cent. starch, equal to 1445 kilos.).

Märker states that potatoes rich in starch should be used for seed. Samples of a Saxon variety of potatoes were analysed, and a great difference was found in the amount of starch present. In experimenting on the effects of different manures on the potato, it was shown that the produce was increased with potassium salts, especially the chlorides, whilst the amount of starch was diminished. Märker strongly condemns the manufacture of starch without the utilisation of the refuse water for the irrigation of meadows and arable land, as this water contains valuable fertilisers.

According to Saare, the great loss in the manufacture of starch is due to the want of efficient disintegrating machines. D. B.

**Experiments with Nielsen and Petersen's Centrifugal Separator.** By W. FLEISCHMANN (*Bied. Centr.*, 1883, 411—415).—A description of the machine and some results of working with it; the yield of cream is good; and rate of revolution being but 1600 revolutions per minute against 4232 revolutions in the Laval separator, there is considerably less danger of accident. In eight experiments, where the temperature of the milk was gradually increased from 5° to 40°, the fat left in the skim milk decreased from 0·8508 in the first to 0·2229 in the eighth, which the author takes to prove the beneficial influence of a temperature of 40°. Suggestions are made for improvements or additional appliances, but would not be understood without a long description. J. F.

**Comparison of Various Systems of Butter-making.** By N. FJORD and others (*Bied. Centr.*, 1883, 415—416).—The authors have for a year compared five different systems of butter-making: the ice process; cooling by water at 10°; churning; and the centrifugal machine of Nielsen and Petersen. The yield from all processes varied considerably, but the centrifugal showed the best; and whereas the average of the ice process required 27·5 lbs. of milk to make 1 lb. of butter, the centrifugal required 3 lbs. of milk less. J. F.

**Faults in Butter Manufacture.** By OTTO (*Bied. Centr.*, 1883, 417).—The author draws attention to certain precautions which should be taken not only in butter-making, but with the milk from which butter is made, as many mistakes do not show themselves until after the butter has been stored some time.

Cows should not be irrationally fed; they should not be constantly fed on one material, but on various descriptions of fodder in reasonable variety. The milk of old cows which is slightly bitter should only be used in moderate proportion with other milks. Ventilation of stables must be carefully attended to, the cows kept clean, and the milk quickly removed from the stable lest it should acquire a bad flavour. The locality of the dairy should be carefully attended to. A free



current of fresh air should play around it, and the floor should not be made of a porous material, such as bricks. The cleansing of the vessels is of the greatest importance. The rancidity of butter is frequently due to want of attention to this; they should be cleaned with soda, steam, &c. The souring of the cream should not be continued longer than 24 hours, or the butter will have a slightly bitter taste.

J. F.

**Fixing Indigo on Cotton.** By SCHLIEPER and BAUM (*Chem. News*, 48, 64—65).—For this purpose, the indigo is ground up for two days with caustic soda and water; it is then mixed with a mixture of British gum, maize starch, water, and caustic soda, and the whole heated at 55° in a water-bath, well stirred, and cooled immediately. The colour ought now to be gelatinous, and is printed on the cloth, which is prepared with glucose and well dried. The dyed cloth is then steamed for 10—15 minutes. Light or dark shades are obtained by using more or less indigo with more or less soda. The *only good resist* is precipitated sulphur, and thickening. A *yellow resist* is formed with cadmium chloride, precipitated sulphur, and thickening. A *red resist* is made of red liquor, tin-crystals, calcined starch, and precipitated sulphur. *Light blue*, the cloth prepared with glucose, is printed with caustic soda, thickened with dextrin and maize starch, steamed for 15 seconds, and padded with indigo colour. In using the red resist, the soda must be removed, or the cloth must be passed into ammonium chloride. An indigo colour is easily discharged on Turkey-reds. For a Turkey-red mordant, heat gelatinous alumina with caustic soda, add water, neutralise with hydrochloric acid, and add more water. For padding, this mixture is also used in a more dilute form; it is dried and aged on the cloth, then passed through lukewarm chalk water, which converts the sodium into calcium aluminate. This mordant can withstand the action of sulphuric acid without losing much of its depth, and on this property the production of indigo discharge styles is founded. For the production of indigo Turkey-red, the cloth previously mordanted for, or dyed with alizarin, is saturated with glucose. The indigo is now printed on, the fabric steamed, washed, exposed to the air for a few minutes, passed into sulphuric acid (8° B.) for about 20 seconds, washed, passed into weak sodium carbonate, and again washed. The red pieces are soaped at a boil, the alizarin is dissolved, and the blue colour appears. To obtain white on Turkey-red or indigo-blue, a dark blue and strong soda-lye are printed on before proceeding as indicated, or a strong lye is printed on the Turkey-red mordant, then steam, dry, and print on the indigo.

D. A. L.

**Process for preparing a Mineral White.** (*Dingl. polyt. J.*, 248, 260).—According to Cobley, a solution of magnesium sulphate is converted into magnesium chloride by the addition of calcium chloride. 10 per cent. of aluminium chloride are then added. Calcium hydroxide throws down a white precipitate from the mixed solution. A cheaper white is obtained by precipitating a solution of the corresponding sulphates with calcium hydroxide.

D. B.

## General and Physical Chemistry.

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**Photographic Investigations of the Ultra-Violet Spark Spectra emitted by Metallic Elements and their Combinations under Varying Conditions.** By W. N. HARTLEY (*Chem. News*, 48, 195—196).—It has been shown (*Brit. Assoc. Jour.*, 1882) that the spectra of metallic solutions are the same as those from metallic electrodes, the principal difference being that short lines in the spectra from the metals become long in the spectra from solutions, whilst very short lines sometimes disappear, as for example in the case of zinc. This is probably due to the solution not being able to contain a sufficient quantity of metal to yield an image of them: thus the very short lines of the aluminium spectrum are not reproduced in solutions of the chloride unless the solutions are extremely concentrated. With regard to the short lines being lengthened by moistening iridium electrodes with calcium chloride, it has now been shown that moistening with water has the same effect: hence the supposition that a chloride of the metal was formed is untenable. The very short lines in the zinc spectrum are also lengthened by moistening the electrodes with water. This variation in the spectra appears to be due to the cooling action of the water on the negative electrode, since heating the electrodes produces a reverse result. Carbon gives two spectra in air when dry, and a third when moistened with water; the three have been photographed, but cannot be exactly described without maps. Numerous experiments have been tried to determine which non-metallic elements are capable of yielding spark spectra when they are combined with metals. Chlorides, bromides, iodides, sulphides, nitrates, sulphates, selenates, phosphates, carbonates, and cyanides yield none. Hydrochloric acid solutions of arsenites, arsenates, and antimonates yield spectra of arsenic and antimony respectively, and solutions of borates and silicates yield characteristic spectra (see below) of the non-metallic constituents; even if sodium salts are employed no metallic lines appear in the case of borates, and with silicates only the strongest sodium line ( $\lambda = 3301$ ) is visible, even in concentrated solutions.

Spark.		Carbon spectra lines (Liveing and Dewar).	
Boron (wave-lengths).	Silicon (wave-lengths).	Spark.	Arc.
3450·1	2881·0	—	2881·0
2497·0	2631·4	2541·0	—
2496·2	2541·0	2528·2	2528·1
	2528·1	2523·6	2523·9
	2523·5	2518·7	2518·8
	2518·5	2515·8	2515·8
	2515·5	2514·0	2514·1
	2513·7	2506·3	2506·6
	2506·3		2478·3
	2435·5		2434·8

It will be observed that these silicon lines are identical with those (annexed table) attributed by Liveing and Dewar (*Proc. Roy. Soc.*, **33**, 403) to carbon, and from many hundred spectra taken between graphite poles it is apparent that in the arc spectrum carbon yields but one line (2478·3 wave-length) in the ultra-violet.

The ultra-violet spectrum of beryllium has been obtained from the solution of its chloride, and the following lines were observed:—

Wave-lengths.	Description.
3320·1	Strong, sharp.
3129·9	Very strong, extended.
2649·4	Strong, sharp.
2493·2	Strong, sharp.
2477·7	Strong, sharp.

From these observations and the general grouping of the lines, the author feels inclined to regard beryllium as the first member of the dyad series to which barium, calcium, and strontium belong. Reasons are given for not classing beryllium with other metals.

D. A. L.

**Production of Electricity by Condensation of Aqueous Vapour.** By S. KALISCHER (*Ann. Phys. Chem.* [2], **20**, 614—620).

—The production of electricity by condensation of aqueous vapour presents a problem of considerable meteorological importance as regards the origin of atmospheric electricity. It is, however, probable that the production of electricity observed is in most cases due to the friction between the water particles and the condensing surface. In this paper the problem is examined experimentally by means of an apparatus which permitted the condensation of aqueous vapour by cooling. It consisted essentially of a series of beakers filled with ice, and covered externally with tinfoil; the beakers were placed on a plate of galvanised iron connected with a quadrant electrometer, and the whole combination was enclosed in a metallic box. Although deviations of the needles of the electrometer were observed, yet they were of the same magnitude and direction whether the beakers were filled with ice or not; and secondly, they were sometimes in one, and sometimes in the other direction.

Other experiments are described in which air was compressed in, and then allowed to expand from a vessel resembling the electric egg, the metallic stopcock of which was in connection with a quadrant electrometer. But in this case, although a pressure of 25 atmospheres was used, and the aqueous vapour fell in the form of fine dew on releasing the pressure, yet there was no development of electricity.

V. H. V.

**Measurement of the Quantity of Electricity produced by a Zamboni's Pile.** By E. RIECKE (*Ann. Phys. Chem.* [2], **20**, 512—524).—This paper contains a series of determinations in absolute measure of the quantities of electricity produced by three Zamboni's piles containing a large number of platinum plates interposed between strips of silk. A long series of tables of those quantities obtained on days of different relative humidity are given, and formulæ

for their calculation as well as for differences of potential are also quoted. V. H. V.

**Influence of Galvanic Polarisation on Friction.** By K. WAITZ (*Ann. Phys. Chem.* [2], 20, 285—303).—In 1874 Edison noticed that the friction between a metallic and a porous plate moistened with some conducting liquid, was diminished when an electric current was sent through this combination from the porous to the metallic plate. Further changes in the friction are produced by variations in the intensity of the current. This fact has been practically applied in the construction of telephones and electromotographs.

In this memoir the phenomenon is more completely investigated. The apparatus consists in the main of a clay cylinder filled with acidulated water, and enclosed within a glass vessel filled with water of the same concentration. A platinum foil is introduced into the inner, and a strip of glass in the outer vessel, on which a small platinum foil is stretched; this latter is connected with a mechanical arrangement whereby the platinum foil on the glass strip can be pressed against the clay cylinder with various degrees of pressure. The whole arrangement is enclosed in circuit with two Daniell's cells, a metallic arrangement to measure the degree of pressure, and a rheostat to vary the intensity of the current. In many experiments it was found that the friction between the platinum and the porous cell is materially diminished when the intensity of the current is sufficient to decompose the acidulated water.

As the contact of the platinum and the clay was not found to be sufficiently perfect, a polished glass cylinder was substituted. The alteration of friction between glass and various metals, platinum, palladium, gold, and nickel, introduced into such solutions as sulphuric acid, potash, and soda, and potassium ferrocyanide was carefully examined: in the original memoir extensive tables are given of the results obtained in the course of the investigation. As a general result it may be stated that there is a diminution of resistance when the metallic plate is the anode, but an increase when the plate is the kathode, and the intensity insufficient to decompose the electrolytic liquid. This latter fact is contrary to the experience of Koch, who found no alteration in the case of the kathode. As the diminution of resistance appears only when bubbles of gas appear at the surface of the plate, it appears probable that the occlusion of the gas by the electrode is the cause of the phenomenon. Another hypothesis is that the formation of an electric double stratum, called forth by the polarisation on the surface of the electrodes, alters the external friction between the metallic surface and the glass on the one hand, and the glass and the liquid on the other.

Further experiments will decide between these two hypotheses, but the writer inclines to the latter. V. H. V.

**Relations between Coefficients of Friction and Galvanic Conduction.** By E. WIEDEMANN (*Ann. Phys. Chem.* [2], 20, 537—538).—In connection with a remark of G. Wiedemann on certain rela-

tions existing between coefficients of friction and galvanic conduction, and the theoretical deductions drawn therefrom, a series of investigations has been made on this point. However, in order to prove how far these relations hold good, the author examined solutions of crystalline zinc sulphate in water and aqueous glycerol of various concentrations. The coefficients of friction were measured by Spring's apparatus, those of conduction by a Wheatstone's bridge.

Strength of solution $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ .	Ratio of coefficient of friction		Ratio of coefficient of conduction	
	In water.	In glycerol.	In water.	In glycerol.
1 per cent.....	1	68.7	1	12.1
2 „ .....	1	29.8	1	9.52
5 „ .....	1	6.5	1	3.68

These numbers show that the ratios existing between the coefficients of friction and conduction are not simple, and further that the nature of the solvent and also its concentration exert a most marked influence on them.

V. H. V.

**Galvanic Temperature Coefficient.** By V. STOUHAL and C. BAROS (*Ann. Phys. Chem.* [2], 20, 525—536).—Previous researches have not established any differences of specific resistance as factors of the temperature corresponding to known differences of composition of various forms of iron and steel. It appeared, however, probable to the writer that iron, whose coefficient of resistance varies according to its degree of hardness and temper, should also possess various temperature coefficients. In this connection it has been shown by Matthiessen and Vogt that the temperature coefficients of platinum-silver alloys decrease with the proportion of platinum; like differences have been observed by the authors in the case of German silver. Similarly it is to be expected that iron, containing various proportions of carbon, which may function as the second metal, should display similar variations. Experiments were accordingly made on steel tempered at various “heats,” and specimens of bar and pig-iron.

In the case of steel the temperature coefficient of the steel varies as its coefficient of resistance continuously with the hardness of the steel, and decreases with increase of the temperature at which it is tempered.

The experiments of Matthiessen and Vogt on bar-iron, and those quoted in this memoir on pig-iron, show that the temperature coefficient varies with the proportions of carbon, and further, that the specific resistance of the latter is far greater than that of the hardest steel.

The above observations point to a marked analogy existing between alloys and steel in their galvanic relations, and to a general law that in all cases of homogeneous substances differences of specific resistance cause similar differences of temperature coefficients, increments of the former corresponding to diminutions of the latter. In alloys it is the small proportion of added metal which raises the specific re-

sistance, in steel the carbon produces the same effect. It is also most probable that the magnetic, as the galvanic, temperature-coefficients vary with the degree of hardness in the same way.

Other experiments are also promised on the analogy existing between alloys and steel as regards their physical properties.

V. H. V.

**Dependence of the Boiling Point on Pressure.** By G. W. A. KAHLBAUM (*Ber.*, **16**, 2476—2484).—It has usually been assumed that a diminution of pressure of 1 cm. lowers the boiling point  $1^{\circ}$ . Experiments made in an apparatus in which the pressure could be kept constant whilst a considerable amount of liquid distilled, showed that this assumption is quite erroneous. The experiments were mainly for pressures of 5—100 mm. The nature of the variations is best shown by the results obtained with some of the fatty acids.

Formic acid.			Propionic acid.			Butyric acid.		
mm. Pressure.	Boiling point.	Sp. R.	mm. Pressure.	Boiling point.	Sp. R.	mm. Pressure.	Boiling point.	Sp. R.
24·84	21·8°	0·1071	21·31	56·5°	0·112	10·06	63·5°	0·131
27·66	22·6	0·1065	22·46	57·6	0·111	21·48	75·2	0·171
32·58	24·6	0·104	31·34	63·5	0·104	31·94	81·4	0·110
41·40	27·9	0·101	41·70	68·8	0·098	43·12	87·5	0·103
49·66	30·5	0·099	44·20	69·2	0·098	48·90	89·8	0·101
74·54	37·6	0·092	47·30	70·4	0·097	760·00	161·5	—
760·00	100·6	—	760·00	139·4	—	—	—	—

From these results it will be seen that the variations are peculiar to each substance and pressure. The figures in the third column of the tables give the ratio of the diminution of boiling point to diminution of pressure (from the boiling point at 760 mm.), termed by the author the *specific remission*. On obtaining by means of curves the specific remission for 0 mm. pressure, it appears that for the substances experimented with (lower fatty acids, alcohols, and anhydrides) a difference in the composition of  $\text{CH}_2$  corresponds with a difference of 0·01 in the specific remission for 0 mm. pressure.

A. J. G.

**Heat of Combination of Carbon and Oxygen.** By A. BOILLOT (*Compt. rend.*, **97**, 490—491).—Thermochemical investigations should determine the quantity of heat due to each individual constituent entering into combination or being liberated by decomposition, but, up to the present the determinations made measure only the sum or the difference of the effects due to the different constituents. In the combination of carbon and oxygen, how much heat is developed or absorbed by the carbon and oxygen respectively? Let A be the heat developed by the combination of 2 vols. of oxygen (weighing 2·666) with 2 vols.\* of carbon vapour (weighing 1) to form 2 vols. of car-

\* The volume ratios and weights are given as in the original paper.

bonic anhydride (weighing 3.666), B the heat developed by 1 vol. of oxygen combining with 2 vols. of carbonic oxide to form 2 vols. of carbonic anhydride, then  $A - B$  will be the heat developed by the union of 1 vol. of oxygen with 2 vols. of carbon vapour with formation of 2 vols. of carbonic oxide. Let  $x$  be the heat absorbed by the unit weight of carbon passing into the state of vapour occupying 2 vols., then  $A - B + x$  will be the heat furnished by 1 vol. of oxygen combining with 2 vols. of carbon vapour to form 2 vols. of carbonic oxide, and  $A - B + x = B$ , whence  $x = 2B - A$ .

Using 6 grams of diamond, the results will be  $A = 47$  cal.,  $A - B = 12.9$  cal.,  $B = 34.1$  cal., and  $x = 21.2$  cal.  $A + x = 68.2$  cal. will be the total heat furnished by the combination of 2 vols. of oxygen (weighing 16 grams) with 2 vols. of carbon vapour (weighing 6 grams) to form 2 vols. of carbonic anhydride (weighing 22 grams). Of these 68.2 cal., 21.2 cal. are absorbed by the carbon.

C. H. B.

**Sodium Alcoholates.** By DE FORCRAND (*Compt. rend.*, **97**, 108—111).—The heats of solution of the three known alcoholates in water at  $20^\circ$  are as follows:—

$C_2H_5NaO$ , solid	+ 13.47 cal.
$C_2H_5NaO, 2C_2H_6O$ , solid	+ 10.46 „
$C_2H_5NaO, 3C_2H_6O$ , solid	+ 12.34 „

and the heats of formation are therefore—

$2C_2H_6O$ , liquid, + $Na_2O$ , solid, = $C_2H_5NaO$ , solid, + $H_2O$ liquid	develops + 34.70 cal.
$C_2H_6O$ , liquid + $NaHO$ , solid, = $C_2H_5NaO$ , solid, + $H_2O$ liquid	„ + 0.25 „

It would appear, therefore, that the heat of formation of sodium alcoholate from sodium hydroxide, like that of sodium glycollate, is practically *nil*.

$C_2H_5NaO$ , solid + $2C_2H_6O$ , liquid, = $C_2H_5NaO, 2C_2H_6O$ , solid	develops + 8.06 cal.
$C_2H_5NaO$ , solid + $3C_2H_6O$ , liquid, = $C_2H_5NaO, 3C_2H_6O$ , solid	„ + 8.64 „
$C_2H_5NaO, 2C_2H_6O$ , solid + $C_2H_6O$ , liquid, = $C_2H_5NaO, 3C_2H_6O$ , solid	„ + 0.58 „

A considerable proportion of this development of heat is due to the solidification of the alcohol. The inverse reactions give—

$C_2H_5NaO$ , solid + $H_2O$ liquid = $C_2H_6O$ liquid, + $NaHO$ solid	+ 1.19 cal.
$C_2H_5NaO, 2C_2H_6O$ , solid, + $H_2O$ liquid = $3C_2H_6O$ liquid + $NaHO$ , solid	— 6.82 „
$C_2H_5NaO, 3C_2H_6O$ , solid + $H_2O$ liquid = $4C_2H_6O$ liquid + $NaHO$ , solid	— 7.44 „

The decomposition of the alcoholates by water in excess takes place

by reason of the development of heat which accompanies the hydration of the two products of the reaction, a development which amounts to + 17.78 or + 19.78 cal., according as the amount of alcohol is  $3\text{C}_2\text{H}_5\text{O}$  or  $4\text{C}_2\text{H}_5\text{O}$ . From these data it follows that  $\text{C}_2\text{H}_5\text{O}$  liquid + Na solid =  $\text{C}_2\text{H}_5\text{NaO}$  solid + H gas develops + 32.13 cal., a number very similar to that developed by the action of sodium on water. Direct determination of the heat developed by the action of sodium in a large excess of alcohol gives the heat of solution of the anhydrous alcoholate in excess of alcohol as 12.65 cal., a value closely approaching the heat of solution of sodium hydroxide by water.

These results show that water and alcohol have almost equivalent functions with respect to sodium and sodium oxide. This fact and the dissociation of the secondary hydrates and alcoholates explain the equilibrium which is established in liquids containing alcohol, water, and sodium oxide. C. H. B.

**Aqueous Solution.** By J. A. GROSHANS (*Ann. Phys. Chem.* [2], 20, 492—512).—The sp. gr. of an aqueous solution of 1 mol. of a substance in 4 mols. of water can be expressed by the interpolation formula  $a = 1 + \frac{aa}{18(A + \lambda)}$ , in which  $a$  is the molecular weight of the

substance, 18 that of water,  $\alpha$  is a constant, and  $\lambda = \frac{\alpha}{18\beta}$ , where  $\beta$  is another constant. In this communication, certain relations existing between  $aa$  for the haloid salts and the nitrates of certain metals are brought out. Thus, for example, the differences of the values for  $aa$  for the iodide and bromide of strontium is equal to the difference between the same values for the iodide and bromide of magnesium. The same difference exists between the values for the bromides and chlorides of magnesium and cadmium. A few examples are quoted below:—

	Value for $aa$ .		Value for $aa$ .
SrI <sub>2</sub> .....	283.85	MgI <sub>2</sub> .....	226.93
SrBr <sub>2</sub> .....	211.37	MgBr <sub>2</sub> .....	152.38
	<hr/> 72.48 <hr/>		<hr/> 74.55 <hr/>
MgBr <sub>2</sub> .....	152.38	CdBr <sub>2</sub> .....	226.93
MgCl <sub>2</sub> .....	78.47	CdCl <sub>2</sub> .....	152.38
	<hr/> 73.91 <hr/>		<hr/> 74.53 <hr/>

Hence it follows, for these salts, that  $R(\text{I}_2 - \text{Br}_2) = R(\text{Br}_2 - \text{Cl}_2) = \text{I}_2 - \text{Br}_2 = \text{Br}_2 - \text{Cl}_2 = 73.80$ . Similarly these differences for  $aa$  are the same, not only for the non-metallic but also for the metallic radicles. Thus  $\text{Pb} - \text{Ba} (aa) = \text{Cd} - \text{Mg} (aa) = 72.48$  to  $74.55$ : so also  $\text{Ba} - \text{Sr} = \text{Sr} - \text{Ca} = 43.15$ . A series of analogous differences is quoted in this memoir, derived not only from the above formula, but also from modifications of it in which other constants



are introduced. The compounds more especially investigated are the halogen acids and their salts together with the nitrates of the alkaline earth and the magnesium-zinc-cadmium-group. V. H. V.

**Specific Gravity of Normal Salt Solutions.** By C. BENDER (*Ann. Phys. Chem.* [2], 20, 560—578).—Valson has noticed (*Compt. rend.*, 73 and 77) certain differences existing between the sp. grs. of metallic salts containing 1 gram of salt in 1 litre. For example, there is a constant difference between the sp. grs. of the potassium and ammonium salts, whatever be the non-metallic radicle associated with them, and, conversely, there is a constant difference between the sp. grs. of the chlorides and nitrates, whatever be the metallic radicle. So that to each metallic and non-metallic radicle there can be assigned a certain value or modulus with which it may be said to enter into solution. The following table explains the above statement:—

	Cl.	Br.	I.
K.....	1·0444	1·0800	1·1135
NH <sub>4</sub> .....	1·0157	1·0520	1·0847
	<hr/> 0·0287	<hr/> 0·0280	<hr/> 0·0288
	K.	Na.	NH <sub>4</sub> .
NO <sub>3</sub> .....	1·0591	1·0540	1·0307
Cl.....	1·0444	1·0396	1·0157
	<hr/> 0·0147	<hr/> 0·0144	<hr/> 0·0150

If, then, the sp. gr. of one salt, preferably that of ammonium chloride as the lowest, be taken as a standard, then the sp. gr. of other salts can be deduced from it by means of the equation  $d = d_a + m_b + m_s$ , in which  $d_a$  is the sp. gr. of ammonium chloride, and  $m_b, m_s$  the moduli of the metallic and non-metallic radicle respectively. Valson has also observed that similar relations exist between the refraction equivalent of the metallic salts.

From these facts, the following general law may be deduced:—*Elements or radicles, entering into combination, are endowed with certain physical constants which are independent of the chemical nature of the resultant compounds.*

It is, however, pointed out that these observations were restricted to salt solutions of the same strength, and presupposes the same coefficient of expansion for each of the salt solutions.

In this paper these observations are extended to solutions containing one or more molecules of salt; it is shown that the modulus (*vide supra*) divided by the number of molecules in solution is a constant. This statement is explained by the table below, in which  $\mu$  represents the number of molecules and  $\Delta$  the modulus:—

$\mu$ .	NH <sub>4</sub> Cl.	KCl.	$\Delta$ .	$\frac{\Delta}{\mu}$	NaCl.	$\Delta$ .	$\frac{\Delta}{\mu}$
1..	1·0157	1·0444	287	287	1·0401	244	244
2..	1·0308	1·0887	579	289	1·0788	480	240
3..	1·0451	1·1317	866	289	1·1164	713	238

A series of analogous examples of a large number of metallic salts is given in the original memoir; some of the values for the modulus in  $\frac{1}{100000}$  units at  $0^\circ$ , deduced from various experiments, are given below:—

Metal.	$\Delta$ .	Element or Radicle.	$\Delta$ .
NH <sub>4</sub> .....	0	Cl. ....	0
K .....	289	Br .....	373
Na .....	238	NO <sub>3</sub> .....	163
Li .....	78	(SO <sub>4</sub> ) <sub>2</sub> .....	206
$\frac{1}{2}$ Ba .....	735	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .....	-15
$\frac{1}{2}$ Sr .....	500		
$\frac{1}{2}$ Mg .....	210		
$\frac{1}{2}$ Mn .....	356		
$\frac{1}{4}$ Zn .....	410		
$\frac{1}{2}$ Pb .....	1087		

From these data the following will be the general equation for calculating the sp. gr. of a salt solution containing  $\mu$  molecules in solution:  $d\mu = d(\mu)\sigma + \mu(m_b + m_s)$ , in which  $d\sigma$ ,  $m_b$ , and  $m_s$  represent the same values as in the equation above. Attention is drawn to the general interest attached to these relations, and to their wider application to the more complicated organic combinations. V. H. V.

**A New Liquid of High Specific Gravity, Refraction Equivalent, &c.** By C. ROHRBACH (*Ann. Phys. Chem.* [2], 20, 169—174).—Schaffgotsch, Church, and Klein have proposed various liquids of high sp. gr. for the practical separation of minerals. In the present memoir, a solution of the double salt of barium and mercuric iodide is recommended for this purpose, which forms a highly refractive golden-coloured liquid of sp. gr. 3.575 to 3.588. It boils at about  $145^\circ$ , evolving with the steam red vapours of mercuric iodide. It has the advantage that it neither decompose carbonates, nor absorbs carbonic anhydride from the air, but readily takes up water. Tables are given of various minerals which may be separated by means of this liquid. The following refraction values for Fraunhofer's lines were obtained:—

	C.	D.	E.	F.	$\frac{n_F - n_C}{n_C}$
Barium mercuric iodide sp. gr. = 3.564 .....	1.7754	1.7930	1.8065	1.8488	0.409

G and the following Fraunhofer's lines could not be measured, owing to strong absorption in the violet. The high dispersive power of the liquid is also shown by the well-defined separation of the two D lines  $nD_1$  and  $nD_2$ . This liquid may possibly be available for other mineralogical and physical investigations. V. H. V.

**Compressibility of Gases.** By E. H. AMAGAT (*Ann. Chim. Phys.* [5], 28, 456—464).—The author contradicts Caillietet's statements (*Ann. Chim. Phys.* [5], 19), (1) that mercury absorbs oxygen at the

ordinary temperature; (2) that glass manometers are distended by pressure to such an extent as to affect the accuracy of the author's determinations of the compressibility of gases (*ibid.* [4], 29).

W. C. W.

**Compressibility of Air and Carbonic Anhydride at 20–300° under 1 to 8 Atmospheres' Pressure.** By E. H. AMAGAT (*Ann. Chim. Phys.* [5], 28, 464–480).—In order to avoid the disturbing influence arising from the tension of the vapour of mercury, a special apparatus was constructed in which the gas does not come into immediate contact with the mercury during the determination.

Air obeys Marriotte's law under a pressure of 8 atmospheres at temperatures between 20° and 300°.

Carbonic anhydride deviates from the law, but the deviation diminishes as the temperature increases, *e.g.*, the value of  $\frac{pv}{p'v'}$  at 50° to 300° under different pressures is shown in the following table:—

Pressure cm.	50°.	cm.	100°.	cm.	200°.	cm.	300°.
74	1·0037	72	1·0027	71	1·0009	72	1·0003
147	1·0075	143	1·0051	141	1·0025	143	1·0015
291	1·0143	282	1·0085	250	1·0041	287	1·0017

W. C. W.

**Compressibility of Rarefied Air, Hydrogen, and Carbonic Anhydride.** By E. H. AMAGAT (*Ann. Chim. Phys.* [5], 28, 480–499).—Gases appear to obey Marriotte's law under low pressures. Under very slight pressures, the errors of experiment are too great to permit any conclusions to be deduced from the determinations.

W. C. W.

**Condensation of Carbonic Anhydride by Glass.** By R. BONSEN (*Ann. Phys. Chem.* [2], 20, 545–560).—The thickness of the layer of carbonic anhydride condensed on the surfaces of the glass is so small, that a very extended surface is required for exact measurement of the amount of gas so condensed. The best material for the examination of this phenomenon is ordinary glass-wool; the sample used in the course of the investigation was of such a degree of fineness, that 150 grams occupied a space of 100 c.c., corresponding with a thread-length of 62 geographical miles, and exposing a surface of 23 square metres. Its sp. gr. was 2·5056. In the original paper the determinations on which these figures are based are given at length. A quantity of this glass-wool was introduced into a gas apparatus, which was filled with perfectly dry carbonic anhydride, and the experiment continued for three years, observations being made from time to time.

The following results are arrived at:—(1) The gas condensation does not reach a fixed point, even after several years; (2) during the continuation of the experiment, notwithstanding instantaneous or continual changes of temperature and pressure, no giving up of the

carbonic anhydride was observable; (3) within temperature of  $+23^{\circ}$  to  $-8^{\circ}$  a rise of temperature produces an acceleration, a fall a corresponding retardation of the absorption. In the three years 5.135 c.c. of carbonic anhydride under standard conditions were absorbed by 1 square metre of the glass wool.

The results of these experiments are in direct contradiction to others on the same phenomenon; this discrepancy is, however, due to the fact that in former experiments the phenomenon was supposed to be finite and not continuous.

As the chemical affinity of the silicic anhydride for the basic substances in the glass is greater than that of the carbonic anhydride, the supposition of a combination of the latter with the glass is precluded; thus it appears that the carbonic anhydride is condensed as such. The long continuation of the phenomenon can be explained by an imperfect interpenetration of the glass by the molecules of the liquid carbonic anhydride. Further experiments will be required to prove whether after a sufficiently long interval of time this interpenetration becomes a sufficiently diminishing quantity; when this point is reached, the conditions remaining the same, neither condensation nor evaporation of the liquid carbonic anhydride would take place, although either one or the other might be caused by a change of the conditions. It would thus be not altogether impossible that for every series of temperatures there would be a corresponding series of levels of the layer of the carbonic anhydride.

It was further found by experiment that atmospheric air behaves towards a glass surface exactly as carbonic anhydride.

V. H. V.

**Similarity of the Behaviour of Ultramarine in a very fine State of Division to that of Metallic Sulphides in the Colloidal State.** By P. EBELL (*Ber.*, 16, 2429—2432).—Ultramarine in a very finely divided state, as it is obtained by grinding and elutriation in the course of its manufacture, shows great similarity in behaviour to the colloidal metallic sulphides described by Spring (*Abstr.*, 1883, 904). The finer parts will remain suspended in pure water for months; the liquid passes unaltered through several thicknesses of Swedish filter paper, does not show any sign of turbidity when examined in a layer 2 cm. thick, and on evaporation leaves the ultramarine in a lustrous layer on the walls of the vessel. Microscopic examination ( $\times 1200$ ) shows only points appearing partly colourless, partly pale blue by transmitted light, deep blue by reflected light. The addition of small quantities of salts, &c., to the liquid causes the separation of the ultramarine: on washing with pure water or very great dilution, the ultramarine passes again into suspension. The author regards it as doubtful if the copper sulphide in the so-called colloidal state is really in solution in water, or whether it is not rather in suspension in a state of division far finer than that in which ultramarine can be obtained by mechanical means.

A. J. G.

**Specific Volumes of Liquid Substances.** By H. KOPP (*Ber.*, 16, 2458—2460).—The author thinks it advisable to call attention to

the fact that in his original paper (*Annalen*, **96**, 155) the relations between composition and specific volume as derived from the observations then accessible were not advanced as being the correct ones, but only as useful approximations.

In comparing the calculated and observed volumes, it is necessary to bear well in mind the real nature of any difference: for instance, taking methyl alcohol (cal. vol. 40·8, obs. 42·1, diff. 1·3) and amyl benzoate (cal. 240·0, obs. 247·7, diff. 7·7), there is not, as at first sight appears, a much greater divergence in the latter case, but in each case the difference is the same, = 3·2 per cent. of the calculated specific volume.

The results obtained by the later experiments with bodies whose relations to one another are now more clearly known, certainly show less agreement with a law of atomic volume than was expected from the earlier experiments; but the agreement of individual substances with many so-called laws is often more general than absolute.

A. J. G.

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## Inorganic Chemistry.

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**Critical Temperature and Pressure of Liquid Oxygen.** By S. WROBLEWSKI (*Compt. rend.*, **97**, 309—310).—When oxygen is liquefied by pressure in a bent tube surrounded by liquid ethylene which is caused to evaporate rapidly, it is found that, as the amount of liquefied oxygen increases so that it rises above the surface of the ethylene, the pressure necessary to continue liquefaction gradually increases, and when the liquid oxygen rises to a certain height in the tube, the meniscus becomes indistinct and finally disappears. These results are due to the fact that the temperature of that part of the tube above the liquid ethylene gradually increases as the distance from the ethylene increases. The disappearance of the meniscus takes place at a pressure of about 50 atmos., and on slightly reducing the pressure the meniscus reappears.

Carbonic anhydride was liquefied by pressure in a tube, the lower part of which was placed in melting ice, whilst the upper part was heated to 50°, the intermediate portions being of course at intermediate temperatures. As the liquefied gas approached the heated portion of the tube, the pressure required to continue liquefaction gradually increased until at about 76 atmos. the meniscus disappeared, but it reappeared on slightly reducing the pressure and consequently reducing the volume of the liquid.

The disappearance and reappearance of the meniscus in both cases evidently takes place at that part of the tube which is at the critical temperature for the particular gas, and the pressure observed at the time of disappearance is the critical pressure. The critical pressure for oxygen is about 50 atmos., and the critical temperature is approximately — 113°.

C. H. B.

**Critical Point of Oxygen.** By E. SARRAU (*Compt. rend.*, **97**, 489—490).—The critical pressure and temperature calculated by means of Clausius' formula from the results of Amagat's experiments on the compressibility of oxygen, are 48·7 atmos., and  $-105\cdot4^{\circ}$  respectively. These values agree fairly well with Wroblewski's determinations (see preceding Abstract). C. H. B.

**Conduct of Moist Phosphorus and Air towards Carbonic Oxide.** By I. REMSEN and E. H. KEISER (*Chem. News*, **48**, 199—201).—In reference to the work of Hoppe-Seyler (*Abstr.*, 1880, 3), Baumann (*ibid.*, 1882, 691), Traube (*ibid.*, 1882, 795), and Leeds (*ibid.*, 1880, 237), on the existence of an active form of oxygen distinct from ozone, the authors have repeated some of the experiments. A repetition of Traube's experiment led the authors to confirm his statement, viz., that the oxidation of palladium-hydrogen is due to the formation of hydrogen dioxide. And again, several repetitions of Leeds's and Baumann's experiments, in which great care was taken to prevent the mixed gases from inside the apparatus coming in contact with organic matter, led the authors to negative Leeds's and Baumann's conclusions; under these conditions no oxidation of carbon monoxide to dioxide took place.

In these experiments all the stoppers were covered with water or mercury, connections were made with pieces of glass tubing bent twice at right angles, so as to avoid india-rubber joints, and all necessary plugs were of asbestos. In some experiments, the asbestos plugs were replaced by cotton-wool, with the result that the gas which previously contained no carbonic anhydride, now precipitated baryta-water; this explains Leeds's error. No satisfactory explanation is given of the negative results obtained by Leeds and Baumann when no carbonic oxide was used. The authors are of opinion that the action of air and moist phosphorus on carbonic oxide furnishes no evidence of the existence of the so-called active oxygen. D. A. L.

**Atomic Refraction of Sulphur.** By R. NASINI (*Gazzetta*, **13**, 296—311).—Brühl's labours on atomic refraction have shown that the same element may have different atomic refractions according to its mode of union with the other elements, but up to the present time the atomic refraction of sulphur in its various compounds has not been made the object of special study.

After noticing what has been already done in determining the refractive indices of various sulphur compounds, the author points out that the questions he proposes to solve are:

1. To ascertain the value of the atomic refraction of sulphur corresponding with oxygen, where bivalent sulphur is united with two univalent groups, as in the mercaptans.

2. Its atomic refraction where the two valencies of sulphur are satisfied by the same carbon-atom.

3. To ascertain whether a variation in valency has any influence on its atomic refraction, by a study of inorganic sulphides and derivatives of carbon acids in which the sulphur is quadrivalent or sexavalent.

The experiments were all made with liquids: these for the most part were supplied by Kahlbaum, but were purified before the determinations were made. The author employed the empirical formula  $\frac{n-1}{d}$  used by Landolt and Brühl, as being but little affected by variations of temperature. H. A. Lorentz and L. Lorenz have recently shown (*Wied. Ann.*, **9**, 64, and **11**, 70) that the formula  $\frac{n^2-1}{n^2+2d}$  is the correct expression for the refractive power of a substance; it gives excellent results, and has also been used by the author. The values for this formula, calculated by Landolt from Brühl's numerous experiments, are given in the subjoined table, where  $r_\alpha$  and  $r_A$  represent the atomic refractions of the elements with respect to the line  $\alpha$  of the hydrogen spectrum, and with respect to the constant A of Cauchy's formula as functions of the old formula  $\frac{n-1}{d}$ ; and  $r'_\alpha$  and  $r'_A$  the same values for the new formula.

		$\frac{n-1}{d}$		$\frac{n_2-1}{(n_2+2)d}$	
		$r_\alpha$	$r_A$	$r'_\alpha$	$r'_A$
Carbon	C.....	5.0	4.86	2.48	2.43
Hydrogen	H.....	1.3	1.29	1.04	1.02
Oxygen (alcoholic)	O' .....	2.8	2.71	1.58	1.56
" (aldehydic)	O'' .....	3.4	3.29	2.34	2.29
Chlorine	Cl.....	9.8	9.53	6.02	5.89
Increment for each double bond.....		2.4	2.00	1.78	1.59

The determinations of the refractive index were nearly all made at 20° with a spectrometer of Bartels and Diederichs, by the method of minimum deviation, using the lines  $\alpha$ ,  $\beta$ , and  $\gamma$  of the hydrogen spectrum and the D sodium line. The sp. gr. of the substance was determined at 20°, referred to water at 4°, reducing it to a vacuum by means of the formula  $d_t = \frac{m}{w}(2-\lambda) + \lambda$ , where  $m$  is the weight of the substance at a temperature  $t$ ,  $w$  that of the water at the same temperature, and  $\lambda$  the mean density of the atmosphere.

The substances examined were ethyl mercaptan, EtHS; ethyl sulphide, Et<sub>2</sub>S; ethyl bisulphide, Et<sub>2</sub>S<sub>2</sub>; isobutyl mercaptan, C<sub>4</sub>H<sub>9</sub>.SH; ethyl monothiocarbonate, OC(OEt)(SEt); isopentyl mercaptan, C<sub>5</sub>H<sub>11</sub>.SH; isopentyl sulphide, (C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>S; diethyl dithiocarbonate, OC(SEt)<sub>2</sub>; carbon bisulphide, CS<sub>2</sub>; the compound, CS(OEt)<sub>2</sub>; sulphurous anhydride, SO<sub>2</sub>; and sulphuric acid, H<sub>2</sub>SO<sub>4</sub>. The results are given in three tables, and from an inspection of them it appears that the atomic refraction of sulphur, like that of oxygen, has two values, according as the two valencies are satisfied by two different univalent



groups, as in mercaptan, &c., or by the same carbon-atom as in carbon bisulphide. These two values are as follows:—

	$\frac{n-1}{d}$		$\frac{n_2-1}{(n_2+2)d}$	
	$r_a$	$r_A$	$r'_a$	$r'_A$
Sulphur with two single bonds .....	14·10	13·53	7·87	7·65
„ „ a double bond .....	15·61	15·09	9·02	8·84

In the case of the oxygenated compounds of sulphur, it would seem that the atomic refraction has only one value, although it differs considerably from those given above.

It is now established that the atomic refraction of an element may vary, not only as it is more or less closely united with other elements—that is, by single or double bonds—but also that the nature of the atoms or variation in the capacity of saturation of the element may greatly influence the value of the refraction-constant. Comparative researches on other multivalent elements, such as phosphorus and arsenic, will no doubt throw light on this most important question.

C. E. G.

**Basic Sulphates.** By J. HABERMANN (*Monatsh. Chem.*, **4**, 787).—Preliminary Notice.—The basic copper sulphate,  $6\text{CuO} \cdot 2\text{SO}_3 \cdot 5\text{H}_2\text{O}$ , which Reindel obtained as a blue-green precipitate on adding ammonia in sufficient quantity to a boiling solution of normal cupric sulphate (*Gmelin-Kraut*, 6 Aufl., vol. iii, p. 628), is also formed by boiling a solution of the normal sulphate (Pickering, *C. J.*, 1883, Abstr., 853), and the author of the present notice has obtained it by treating the solution of the normal sulphate with ammonia or with sodium carbonate in certain proportions.

Basic sulphates of nickel, cobalt, zinc, and cadmium are formed in like manner with either of these precipitants, but the salts thus obtained are not analogous in composition to the copper salt. Further details are promised.

H. W.

**Action of Potassium Permanganate on certain Sulphur compounds.** By M. HÖNIG and E. ZATZEK (*Monatsh. Chem.*, **4**, 738—752).—In this paper the authors describe a large number of experiments on the action of potassium permanganate on the thiosulphates, sulphites, and sulphides of the alkali-metals, the results of which may be summarised as follows:—

1. The thiosulphates of the alkali-metals are completely oxidised by the permanganate at ordinary temperatures, only in alkaline solution. Whatever may be the concentration of the permanganate solution, the complete oxidation of 1 part sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) requires 1·6366 part potassium permanganate. The

composition of the resulting precipitate is best represented by the formula  $\text{KH}_3\text{Mn}_3\text{O}_6$ .

2. The sulphites of the alkali-metals are completely oxidised at ordinary temperatures both in neutral and in alkaline solution. The quantity of permanganate required for oxidation of 1 part by weight of sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) depends on the concentration of the permanganate solution, being less in proportion as that solution is more dilute. The composition of the resulting manganese precipitate is variable, and likewise depends on the concentration of the permanganate solution.

3. The action of permanganate at ordinary temperatures on the mono- and poly-sulphides of the alkali-metals gives rise to sulphuric acid, trithionic acid, and free sulphur; at the boiling heat all or nearly all the sulphur is oxidised to sulphuric acid. H. W.

**Direct Union of Nitrogen and Hydrogen.** By H. B. BAKER (*Chem. News*, **48**, 187—188).—This communication is a reply to Johnson (*Trans.*, 1881, 128, 130). The author describes various experiments with Johnson's and other apparatus, and ultimately comes to the conclusion that nitrogen prepared from air, either by the removal of the oxygen by cold phosphorus, or by potassium pyrogallate, or by hydrogen in the presence of warmed platinum sponge, does not combine directly with hydrogen to form ammonia. When, however, the hydrogen was passed through a solution of silver nitrate, and subsequently through three bottles containing a saturated solution of ferrous sulphate, the author always obtained a brown coloration in the second Nessler tube.

*Note.*—Johnson has discontinued the use of silver nitrate for the purification of his hydrogen (*Chem. News*, **48**, 202). D. A. L.

**Nitrogen Iodides.** By A. GUYARD (*Compt. rend.*, **97**, 526—531).—Nitrogen iodide in contact with water or aqueous ammonia is as sensitive to luminous vibrations as to calorific, sonorous, or material vibrations. When exposed to light, the iodide is rapidly decomposed with effervescence and gives off pure nitrogen, ammonium iodide and a small quantity of ammonium iodate being also formed. In presence of water, the decomposition usually terminates in a violent explosion, but in presence of ammonia it proceeds quietly to the end. Nitrogen iodide is as sensitive to diffused light as to direct rays, the rapidity of decomposition being proportional to the intensity of the light. The decomposition takes place equally well at  $1^\circ$ ,  $5^\circ$ ,  $10^\circ$ , or the ordinary temperature. The infra-red spectrum has no influence on the decomposition, but the visible spectrum acts powerfully, the maximum effect being produced by the yellow rays and the minimum by the violet.

Nitrogen iodide of the composition  $\text{NH}_2$  is decomposed by light in presence of water, without explosion, in accordance with the equation  $2\text{NH}_2\text{I} = \text{NH}_4\text{I}_2 + \text{N}$ . Nitrogen iodide, however, rarely has this composition, and usually contains a greater or lesser proportion of other iodides. The compound therefore generally decomposes at first in accordance with the above equation, but explodes when the iodide,

$\text{NH}_3\text{I}$ , begins to decompose. The decomposition of the typical iodide,  $\text{NHI}_2$ , in presence of ammonia, takes place in accordance with the equation  $5\text{NHI}_2 + 12\text{NH}_3 = 10\text{NH}_4\text{I} + 7\text{N}$ . One and the same nitrogen iodide will give off more nitrogen in presence of ammonia than in presence of water; in the first case ammonium iodide is formed, in the second the diiodide.

The decomposition of nitrogen iodide in ammonia may be used photometrically to determine the chemical and mechanical equivalent of light. The apparatus employed consists of a small flask with a long neck graduated in cubic centimeters, and provided with a stopper. The neck also carries a side tube similar to that of a Gay-Lussac burette. 1.27 gram of iodine is placed in the flask, which is then completely filled with ammonia of  $22^\circ$ , carefully stoppered, with exclusion of air bubbles, and exposed to light. 1.27 gram of iodine gives off 33.5 c.c. of nitrogen. The final reaction is the same whether nitrogen iodide or a mixture of iodine and ammonia is employed, and whether the mixture of iodine and ammonia is exposed to light at once, or time is given for the formation of nitrogen iodide. The decomposition takes place in accordance with the equation  $13\text{NH}_3 + 10\text{I} = 10\text{NH}_4\text{I} + 3\text{N}$ .

*Preparation of Ammonium Iodide and Iodate.*—When a mixture of iodine with excess of ammonia is exposed to light, nitrogen is given off, the free iodine entirely disappears, and ammonium iodide and iodate are formed. The ammonia is driven off and the liquid concentrated, when the ammonium iodide crystallises out, and the iodate remains in solution.

When iodine is mixed with aqueous ammonia, part of the iodine forms ammonium iodide, and the remainder is converted into nitrogen iodide. Afterwards, in presence of light and an excess of ammonia, more ammonium iodide is formed and nitrogen is given off. The first part of the change is chemical, the second photochemical. The principal reaction is represented by Odling's equation  $3\text{NH}_3 + 2\text{I}_2 = 2\text{NH}_4\text{I} + \text{NHI}_2$ . When the iodine is in excess, ammonium diiodide is formed, and the nitrogen iodide produced has approximately the composition  $\text{NH}_2\text{I}$ ; with proper proportions of iodine and ammonia, the nitrogen iodide has approximately the composition  $\text{NHI}_2$ ; with an excess of ammonia, a greater proportion of ammonium iodate is formed. Nitrogen iodide of the composition  $\text{NHI}_2$  is but slightly affected by washing with pure water. Ammonia added to ammonium diiodide forms nitrogen iodide with the second atom of iodine.

Under ordinary conditions,  $x(\text{NH}_4\text{O}) + 233(\text{NH}_4\text{O}) + \text{I}_{303} = \text{NH}_4\text{O}, \text{IO}_3 + 154\text{NH}_4\text{I} + 10(\text{N}_8\text{H}_9\text{I}_{15}) + 227\text{HO} + x(\text{NH}_4\text{O})$ ,\* where  $x\text{NH}_4\text{O}$  represents the excess of ammonia which must always be used, is the simplest equation which expresses the observed facts. The formula  $\text{N}_8\text{H}_9\text{I}_{15}$  is approximately  $8\text{NHI}_2$ . With twice the excess of ammonia, about twice the amount of ammonium iodate is formed, and the nitrogen iodide consists mainly of  $\text{N}_3\text{H}_3\text{I}_3$ , or approximately  $3\text{NHI}_2$ . The formulæ given by previous investigators are probably correct, but refer to bodies prepared under different conditions.

\* This equation is given exactly as it is in the original, it is, however, incorrect, as the two sides are  $\text{N}_{233}\text{H}_{932}\text{I}_{303}\text{O}_{233} = \text{N}_{235}\text{H}_{937}\text{I}_{305}\text{O}_{233}$ .

Nitrogen iodides are decomposed even by very dilute sulphuric, hydrochloric, or sulphurous acid, at first with effervescence, but afterwards with violent explosion. They dissolve in sodium thiosulphate, with formation of sodium iodide, ammonium sulphate, and free ammonia. The free ammonia is that existing in the nitrogen iodide; the ammonium in the ammonium sulphate is derived from the nitrogen existing in the nitrogen iodide in the form of triiodamine. Nitrogen iodide is partially decomposed by potassium iodide in the dark, with formation of potassium diiodide free from ammonia, and a nitrogen iodide insoluble in the alkaline iodide, that is, the iodide  $\text{NHI}_2$  loses an equivalent, or part of an equivalent, of iodine, and yields a new iodide. When exposed to light, however, the nitrogen iodide is completely decomposed by the potassium iodide, and the liquid contains ammonium iodide. Potassium cyanide dissolves nitrogen iodide even in the dark, with evolution of nitrogen.

*Nitrogen Copper Iodide.*—When an ammoniacal solution of a copper salt is mixed with potassium diiodide, a brilliant, crystalline, garnet-coloured precipitate of the composition  $\text{CuI}_2 \cdot 2\text{NH}_3\text{I}$  is gradually deposited. When dried, this compound is very stable, but it is entirely decomposed by water, with formation of ammonium diiodide, and a bronze-coloured cupric oxyiodide,  $\text{CuO}_2\text{I}$ , which is decomposed by heat into black cupric oxide, iodine, and oxygen. The double copper nitrogen iodide is decomposed by aqueous ammonia, with formation of an ammoniacal solution of cupric iodide and a residue of an explosive nitrogen iodide free from copper. When the double iodide is heated, iodine and the products of the decomposition of nitrogen iodide are given off, and a residue of perfectly pure cuprous iodide is left. When distilled, the double iodide yields cuprous iodide, and brown, violet, and ammoniacal vapours. The brown vapours condense to a black product, decomposed by water with formation of a black crystalline nitrogen iodide, which resembles iodine in appearance, but which differs from all the other nitrogen iodides by dissolving with effervescence in a solution of potash or soda, nitrogen or hydrogen being given off, and a considerable quantity of ammonia formed.

When Schweitzer's reagent, prepared by Peligot's method, is mixed with potassium diiodide, a crystalline black double iodide of nitrogen and copper is formed, which resembles the preceding compound in its general properties, but yields an explosive cupreous residue when decomposed by washing with water. C. H. B.

**White Phosphorus.** By I. REMSEN and E. H. KEISER (*Chem. News*, 48, 201—202).—In course of the experiments alluded to in this vol., p. 149, the authors had a suspicion that the phosphorus with which they were working might have contained some carbonaceous matter. To remove this the phosphorus was distilled in an atmosphere of purified hydrogen, and the vapour condensed in cold water. The distilled phosphorus presented a peculiar appearance; it floated on the surface of the water, forming a snow-white layer, and when placed in warm water changed into ordinary phosphorus. After many experiments the authors found that this variety of phosphorus

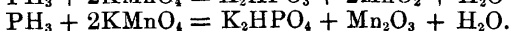
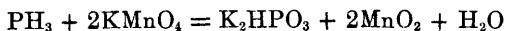
could be prepared in the following manner: Sticks of phosphorus are placed in a tubulated retort, the neck of which is inclined upwards, and projects into a double-necked globular receiver, containing a layer of water and ice  $1\frac{1}{2}$  in. deep in the deepest part. The receiver is supported in a vessel of cold water, and the bent tube, which passes from the other neck of the receiver, dips into cold water. A glass tube is fitted into the tubulure of the retort to supply purified hydrogen, which is passed until the apparatus is filled with it; the current is then stopped, and the distillation proceeded with; this is conducted steadily so that the vapour as it issues from the retort does not condense to a liquid. In successful operations a thin white cake is found floating on the water. The apparatus is allowed to cool, the retort disconnected, and the receiver with its contents put under water to displace the hydrogen and remove the phosphorus; if this precaution is not taken, the phosphorus is liable to take fire, and give rise to an explosion of the mixture of hydrogen and air. White phosphorus is light and plastic; if it is placed on bibulous paper as it dries, it fumes, melts without taking fire, and changes to ordinary phosphorus, with which its melting point is identical. It is soluble in carbon bisulphide, and is not affected by sunlight so readily as ordinary phosphorus; a sample after a year became slightly yellow, but was otherwise unchanged.

D. A. L.

**Reactions of Gaseous Hydrogen Phosphide.** By A. GAVAZZI (*Gazzetta*, **13**, 324—325).—On passing gaseous hydrogen phosphide through a neutral aqueous solution of platonic chloride, an ochreous yellow precipitate of the composition  $\text{PtPH}_2$  is obtained: this is insoluble in water and hydrochloric acid. It ignites when heated to  $100\text{--}110^\circ$ , or when moistened with fuming nitric acid.

Arsenic phosphide,  $\text{AsP}$ , is formed by the action of hydrogen phosphide on a solution of arsenious anhydride in hydrochloric acid.

An aqueous solution of potassium permanganate absorbs hydrogen phosphide at a low temperature, the reaction being represented by the equations—



C. E. G.

**Preparation of Phosphorus Oxychloride.** By E. DERVIN (*Compt. rend.*, **97**, 576—578).—When phosphorus trichloride is mixed with potassium chlorate a violent reaction takes place, phosphorus oxychloride and potassium chloride being formed in accordance with the equation  $\text{KClO}_3 + 3\text{PCl}_3 = 3\text{POCl}_3 + \text{KCl}$ . This reaction may be utilised for the preparation of phosphorus oxychloride. 500 grams of pure phosphorus trichloride free from uncombined phosphorus are placed in a retort of 750—1000 c.c. capacity, connected with an inverted condenser, and 160 grams of finely powdered potassium chlorate is added through the tubulure in quantities of about 4 grams at a time, care being taken to wait each time until ebullition ceases before adding more chlorate. When the whole of the chlorate has been added, the liquid is distilled. The yield is very satisfactory, and the oxychloride contains but mere traces of chlorine.

C. H. B.

**Action of Sunlight on Phosphorous Anhydride.** By A. IRVING (*Chem. News*, **48**, 173).—The author prepared his phosphorous anhydride by passing a slow current of dry air over molten phosphorus, and found that the product turned brown, and changed into free phosphorus and phosphoric anhydride when exposed in sealed tubes to direct sunlight (compare Lewes, *Trans.*, 1884, 10). D. A. L.

**Boron.** By A. JOLY (*Compt. rend.*, **97**, 456—458).—The products of the reduction of boric anhydride by aluminium are: (1.) The boride,  $\text{BAl}$ , which forms golden-yellow hexagonal lamellæ, described by Deville and Wöhler. (2.) The boride,  $\text{B}_2\text{Al}$ , which forms large black lamellæ, analysed by Hampe (*Annalen*, **183**, p. 75). (3.) Yellow quadratic crystals of adamantine lustre containing carbon and aluminium. (4.) A boron carbide, or more probably several carbides formed by the alteration of the preceding compounds, at a high temperature, in presence of carbon and excess of boric anhydride. This carbide forms small black very hard crystals, with a bright metallic lustre, insoluble in boiling nitric acid. They have a sp. gr. of 2.542 at  $17^\circ$ , and contain 15.7 per cent. of carbon, corresponding with the formula  $\text{B}_3\text{C}$ . C. H. B.

**New Silver Compounds.** By T. POLECK and K. THÜMMEL (*Ber.*, **16**, 2435—2448).—Gutzeit has shown (*Pharm. Zeit.*, 1879, 263) that when gases containing arseniuretted hydrogen impinge on a piece of filter-paper moistened in its centre with one drop of a concentrated solution of silver nitrate, the wet spot assumes a lemon-yellow colour, whilst at the periphery a brownish-black ring forms, which slowly broadens towards the centre until the whole spot becomes black. If the spot, whilst still yellow, is moistened with water, it blackens over the whole surface, and at the same time shows a strongly acid reaction. Hydrogen sulphide, phosphide, and antimonide give similar results. The present paper details experiments on the chemical nature of these reactions.

Hydrogen sulphide is passed into a concentrated solution of silver nitrate (1 part  $\text{AgNO}_3$  in 0.7—1.0 part water) kept constantly agitated, when a yellowish-green precipitate of the formula  $\text{Ag}_2\text{S}, \text{AgNO}_3$  is obtained. The supernatant liquid has a strongly acid reaction, does not contain sulphuric acid, and yields a considerable quantity of ammonia when distilled with potash. The precipitate can be heated to  $180^\circ$  without decomposition, and then forms a dark-green powder. It is decomposed into silver nitrate and silver sulphide by treatment with water or alcohol. On oxidation with nitric acid of sp. gr. 1.18 an orange-red coloured powder is frequently obtained. This compound is also obtained by the action of sulphur on a boiling concentrated solution of silver nitrate, and after purification gave results corresponding with the formula  $\text{Ag}_2\text{S}, \text{Ag}_2\text{SO}_4$ . It dissolves in boiling nitric acid, is decomposed by boiling water into silver sulphide and sulphate, and by cold hydrochloric acid into silver sulphide and chloride.

Arsenic trihydride acting on dilute solution of silver nitrate has long been known to yield metallic silver, arsenious anhydride, and

nitric acid; with a concentrated solution, however, the reaction is very different. The first few bubbles of gas produce a deep lemon-yellow coloration, no precipitate is formed, and the liquid acquires an acid reaction; this coloration remains for one or two days, then the liquid becomes colourless, silver is precipitated, and the solution contains arsenious and arsenic acids. If a rapid stream of arsenic trihydride be passed into a concentrated solution of silver nitrate at  $0^{\circ}$ , the whole liquid solidifies to a yellow crystalline mass, but rapidly blackens from separation of silver. Many experiments were tried to isolate the compound, but its instability was too great. Analysis by an indirect method pointed to the formula  $\text{Ag}_3\text{As}_3\cdot 3\text{AgNO}_3$ .

With concentrated solutions of silver nitrate, hydrogen phosphide gave results exactly similar in appearance to those obtained with arsenic trihydride. The composition of the yellow precipitate from indirect determinations was  $\text{Ag}_3\text{P}_3\cdot 3\text{AgNO}_3$ .

A yellow precipitate is also obtained by the action of antimony trihydride on concentrated solution of silver nitrite. It could not be isolated, but indirect determinations gave the formula  $\text{Ag}_3\text{Sb}_3\cdot 3\text{AgNO}_3$ . Unlike arsenic, phosphorus, and sulphur, metallic antimony does not yield the double compound; when it is placed in a solution of silver nitrate,  $\text{Ag}_3\text{Sb}$  is first formed, but is soon converted into antimonious oxide and silver.

A. J. G.

**Silver Nitrite and Ammonia.** By A. REYCHLER (*Ber.*, **16**, 2425—2428).—On dissolving silver nitrite in concentrated aqueous ammonia heat is evolved, and the liquid soon deposits well-formed brilliant yellow prisms of the formula  $\text{AgNO}_2\cdot\text{NH}_3$ , soluble in water, sparingly soluble in alcohol, nearly insoluble in ether, and melting at  $70^{\circ}$ . Long-continued heating above the melting point decomposes the compound, all the ammonia being expelled, and the residue consisting mainly of silver nitrite. On gently heating the compound with ethyl iodide, it yields silver iodide, ethyl nitrite, and ammonia.

On heating the nonammonia compound with alcoholic ammonia and precipitating with ether, the diammonia compound  $\text{AgNO}_2(\text{NH}_3)_2$  is obtained as a white crystalline mass, rapidly losing ammonia on exposure to air.

The finely powdered monammonia compound rapidly absorbs ammonia gas, with considerable evolution of gas, and apparently yields a triammonia compound,  $\text{AgNO}_2(\text{NH}_3)_3$ ; it is readily soluble in water, and rapidly loses ammonia on exposure to the air.

A. J. G.

**Crystallised Calcium Silicophosphate produced in the Dephosphorisation of Iron.** By A. CARNOT and RICHARD (*Compt. rend.*, **97**, 316—320).—The slag formed in working the Thomas-Gilchrist process at Joeuf (Meurthe-et-Moselle) has a brownish or blackish colour, and is more or less crystalline, some parts consisting of transparent crystalline matter, which acts strongly on polarised light, whilst other parts have a reddish colour, and resemble brown hæmatite. The surface of the slag is covered with black crystals, some of which are slender needles, whilst others are right rhombic

prisms with brilliant faces. These crystals are frequently aggregated in columnar masses, which terminate in small vitreous perfectly translucent blue crystals. Similar blue crystals are found in the cavities in the slag, and appear to form one of its principal constituents. These are very constant in composition, but frequently enclose small black needles or particles, which can, however, be removed by means of a magnet. The blue crystals have the composition—

$P_2O_5$	$SiO_2$	$Al_2O_3$	$CaO$	$MgO$	$FeO$	$MnO$	
29.65	12.42	2.76	53.20	traces	1.80	traces	= 99.83.

Vanadium could not be detected. The numbers correspond with the formula  $8P_2O_5, 8SiO_2, Al_2O_3, FeO, 36CaO$ . Regarding the crystals as consisting essentially of calcium silicophosphate, the formula becomes  $P_2O_5, SiO_2, 5CaO$  or  $Ca_3P_2O_8 + Ca_2SiO_4$ . The composition of the crystalline slag is variable; it contains a lower proportion of phosphoric acid than the blue crystals, and a considerable excess of ferrous and manganese oxides.

The calcium silico-phosphate crystals belong to the rhombic system, the angles being  $mm = 113^\circ 10'$  and  $e'e' \text{ (on } p) = 64^\circ$ . They are strongly doubly refractive, and exhibit well-marked dichroism. When the plane of their optical axis is parallel with the principal section of the Nicol's prism, they have a cobalt-blue colour; when it is perpendicular, they are almost colourless.

C. H. B.

**Presence of Yttrium in the Sphene of Biellese Syenite.** By COSSA (*Gazzetta*, 13, 326).—The author has found yttrium and cerium in the sphene of Biellese syenite to the amount of about 2.3 per cent. This is an important fact, as it affords additional evidence of the analogy between the syenite of Biellese and those of Planceuschengrund and Sweden. Besides showing that substances exist in the Alps which were formerly believed to be exclusively confined to Northern Europe, it proves that these rare metals are widely diffused, and their association with calcium compounds may be important in relation to their valency.

C. E. G.

**Separation of Gallium.** By L. DE BOISBAUDRAN (*Compt. rend.*, 97, 295—297, and 521—522).—*From Vanadium.*—(1.) The feebly acid hydrochloric acid solution is mixed with arsenious acid and an excess of acid ammonium acetate, and treated with hydrogen sulphide. Vanadium is not precipitated, but the arsenious sulphide carries down the whole of the gallium. The precipitate is washed with water containing ammonium acetate and hydrogen sulphide, and treated with aqua regia. The arsenic acid is reduced with sulphurous acid, and a current of hydrogen sulphide is passed through the strongly acid liquid, when the arsenic is precipitated alone, all the gallium remaining in solution. This is the only process which gives accurate results when used alone, and it is especially useful for separating small quantities of gallium from large quantities of vanadium. (2.) The



solution is almost neutralised with ammonia, mixed gradually with an excess of ammonium sulphide, and agitated. Dilute hydrochloric acid is then added in considerable excess with constant agitation, and the precipitated vanadyl sulphide is filtered off and washed with dilute hydrochloric acid containing hydrogen sulphide. The filtrate is boiled with aqua regia to destroy ammonium salts, the nitric acid is then expelled, and precipitation repeated six or seven times. The vanadyl sulphide is also dissolved in aqua regia, and reprecipitated several times. (3.) The hydrochloric acid solution is made alkaline with ammonia, and boiled until the liquid is neutral. The precipitate is redissolved and reprecipitated two or three times; the filtrate is treated by method (1) in order to separate the last traces of gallium. (4.) The solution is mixed with sulphuric acid and ammonium sulphate in proper proportions, and the gallium alum is purified by recrystallisation. The solution contains small quantities of gallium.

If the amount of gallium is very small, process (1) is used; if the proportion of gallium is large, and that of vanadium small, the greater part of the gallium is removed in the form of alum, and the mother-liquid is treated by the following method. When the gallium and vanadium are present in approximately equal proportions, the liquid is twice boiled with ammonia (2), and the filtrate treated by (1). The precipitated gallium hydroxide is converted into alum, and the mother-liquor is again boiled with ammonia. The filtrate is treated by (1): the precipitate is mainly converted into gallium alum, and the mother-liquor is finally treated by (1).

*From Tungsten.*—The tungsten is converted into alkaline tungstate, and the solution evaporated almost to dryness at a gentle heat in presence of a considerable excess of hydrochloric acid, a small quantity of water is then added, and the liquid again evaporated almost to dryness. The residue is treated with a moderately large quantity of very dilute hydrochloric acid, gently heated, and the liquid filtered. The filtrate is free from tungsten; the traces of gallium in the precipitate are removed by dissolving it in ammonia, and repeating the process.

*From Phosphoric Acid.*—(1.) The gallium is precipitated by potassium ferrocyanide in presence of a large quantity of hydrochloric acid, and the precipitate is washed with water strongly acidified with hydrochloric acid. (2.) The solution is mixed with about one-third its volume of strong nitric acid, and the phosphoric acid precipitated by means of ammonium molybdate, the gallium and molybdenum being afterwards separated by the method previously described. (3.) The feebly acid solution is mixed with arsenious acid and ammonium acetate, and treated with hydrogen sulphide, as described above.

C. H. B.

**Diffusion of Vanadium in the Mineral and Vegetable Kingdoms.** By L. RICCIARDI (*Gazzetta*, 13, 259—262).—After a recapitulation of the results obtained by various authors on the occurrence of vanadium in rocks and minerals, the author gives the results of his own experiments on the existence of that metal in volcanic emanations ancient and modern. These are as follows, the numbers denot-

ing the percentage of vanadium sesquioxide found in the several substances examined :—

Lava of Vesuvius (1868) .....	0·0063 per cent.
"    "    (1871) .....	0·0075 "
"    "    (1872) .....	0·013 "
Ashes from Vesuvius (1872) ....	0·105 "
Lava of Vesuvius (1881) .....	0·0081 "
Lava of Etna (1669) .....	0·0102 "
"    "    (1879) .....	0·0034 "
Basalt of Pachino .....	0·006 "
Basalt of the Isola dei Cicli.....	0·0084 "

Scacchi has found vanadium in incrustations of the Vesuvian lava of 1631.

E. Bechi (*Atti della R. Accademia dei Lincei* [3], 3, 403 [1878–79]), after having found this element in argillaceous limestones, in schists and in sands, has established its presence in plants, especially in those growing on clay soils.

The author of the present paper has also found it in the ashes of grasses growing on the Etna lava of 1669, but the proportion was too small for quantitative estimation. Its occurrence in plants may be regarded as having some relation to the isomorphism of vanadic and phosphoric acids.

H. W.

**Sulphur Compounds of Molybdenum.** By G. KRÜSS (*Ber.*, 16, 2044—2051).—According to Berzelius, molybdenum forms not only a di- and tri- but also a tetra-sulphide,  $\text{MoS}_4$ , a compound which would point to molybdenum as possessing a quantivalence of eight, and would be analogous to the uranium tetroxide. The author has succeeded in isolating this tetrasulphide by melting molybdic acid with potassium carbonate, exhausting the melt with water, and passing hydrogen sulphide into the solution when heated to the boiling point. A black powder together with a crystalline substance separates out. This mixed material is washed first with cold water, then with hot water to dissolve out the molybdenum di- and tri-sulphide, and the resultant chocolate-brown powder is heated in a current of hydrogen sulphide until its weight is constant. The result of the analysis show that this substance is *molybdenum tetrasulphide*.

The author also describes a series of compounds intermediate between the salts of molybdic and sulphomolybdic acids, which may be designated by the generic term *oxythiomolybdates*.

*Ammonium orthoxythiomolybdate*, prepared by passing hydrogen sulphide into an ammoniacal solution of ammonium molybdate, crystallises in golden-yellow needles of the composition  $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$ , which was assigned to the substance by Debray. The corresponding potassium salt forms reddish-golden needles.

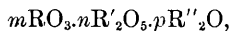
Besides the crystalline orthoxythiomolybdate, a number of amorphous oxysulphomolybdates are obtained by the decomposition of the molybdates by the alkaline hydrosulphide. Ammonium pyroxythiomolybdate, prepared by decomposing ammonium molybdate with ammonium hydrosulphide, is a reddish-golden precipitate having the

composition  $\text{H}_2\text{Mo}_2\text{O}_4\text{S}_3 (= 2\text{H}_2\text{MoO}_2\text{S}_2 - \text{H}_2\text{S})$ , which evidently stands to orthoxymolybdate in the same relation as ortho- to pyro-phosphoric acid. The corresponding sodium salt is a golden amorphous powder.

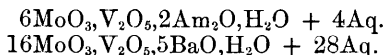
*Thiomolybdates.*—These compounds were obtained by Berzelius by passing hydrogen sulphide into the molybdates and evaporating the liquid; the substances formed by the process are, however, far from pure, owing to a loss of hydrogen sulphide and formation of the oxythiomolybdates. The potassium salt can best be prepared by fusing together potassium carbonate, sulphur, and a large excess of the natural molybdenum sulphide.

*Dithiomolybdates.*—On passing hydrogen sulphide into a solution of potassium molybdate containing a large excess of free alkali, an orange-yellow precipitate separates out; this has the composition  $\text{K}_6\text{Mo}_2\text{S}_9$ , or *potassium dithiomolybdate*. V. H. V.

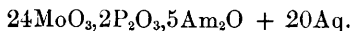
**Complex Inorganic Acids.** By W. GILLES (Chem. News, 48, 155).—Two communications from the author on this subject have already appeared in this Journal (Abstr., 1882, 469, 702). In these communications only binary compounds have been referred to, and these can be represented by the general formula:—



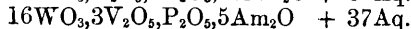
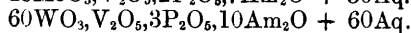
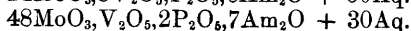
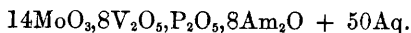
in which  $m$  = any even number from 10 to 48;  $\text{R}$  = either molybdenum or tungsten;  $\text{R}'$  either phosphorus or arsenic; and  $\text{R}''$  the basic radical. He has now extended the generalisation, and states that the phosphorus and arsenic may be replaced by vanadium or antimony, or possibly by niobium and tantalum; for example, well-defined and beautifully crystalline vanadio-molybdates have been obtained having the formulæ:—



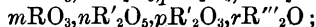
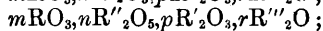
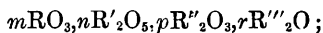
Moreover, the group  $\text{R}'_2\text{O}_5$  may be replaced by the group  $\text{R}_2\text{O}_3$  as  $\text{As}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ , and probably  $\text{V}_2\text{O}_3$ . Thus the formula of an ammonium phosphoroso-molybdate is—



These  $\text{R}_2\text{O}_3$  compounds are converted by oxidation into the salts containing the group  $\text{R}_2\text{O}_5$ . Klein has described salts containing  $\text{R}_2\text{O}_3$ ; salts of this class containing hypophosphorous acid have also been obtained, such as the ammonium hypophosphomolybdate of the formula  $24\text{MoO}_3, 6\text{PO}_2, 6\text{Am}_2\text{O} + 7\text{Aq.}$  There are a great many ternary compounds of a similar character containing molybdic or tungstic oxide united with two other oxides. A great many have the general formula,  $m\text{RO}_3.n.\text{R}'_2\text{O}_5.p.\text{R}''_2\text{O}$ , in which  $\text{RO}_3$  = molybdic or tungstic oxide, whilst  $\text{R}'_2\text{O}_5$  and  $\text{R}''_2\text{O}_5$  = two different oxides of the same type; for example,  $\text{P}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$ . It has not as yet been proved that any two known oxides of the type  $\text{R}_2\text{O}_5$  can enter together into such compounds. The following are some examples of these salts:—

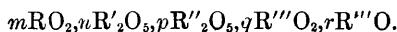


But the compounds containing  $\text{MoO}_3$  or  $\text{WO}_3$  in combination with oxides of two types are still more numerous. They have the following general formulæ:—



in which  $\text{R}_2\text{O}_5$  may be  $\text{P}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$ ,  $\text{As}_2\text{O}_5$ ,  $\text{Sb}_2\text{O}_5$ , and probably  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$ , whilst  $\text{R}_2\text{O}_3$  may be  $\text{B}_2\text{O}_3$ ,  $\text{P}_2\text{O}_3$ ,  $\text{V}_2\text{O}_3$ ,  $\text{As}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ . The author has also prepared salts belonging to the ternary compounds with the general formula  $m\text{RO}_3, n\text{R}'_2\text{O}_5, p\text{R}''_2\text{O}_3, r\text{R}'''_2\text{O}$ . None of this series containing  $\text{R}'_2\text{O}_3$  in place of  $\text{R}'_2\text{O}_5$  have as yet been prepared.

Quarternary compounds also exist, for the author has obtained the following in well-defined crystals:— $60\text{WO}_3, 3\text{P}_2\text{O}_5, \text{V}_2\text{O}_5, \text{VO}_2, 18\text{BaO} + 150\text{H}_2\text{O}$ , which is reducible to the general formula:—



It is evident that the possible number of various combinations in this group is very great. Besides the above types, the author has obtained other compounds containing neither molybdenum nor tungsten; for example: phospho-vanadates, arseno-vanadates, and antimony-vanadates, which are frequently crystalline, and have the general formula  $m\text{R}'_2\text{O}_5, n\text{R}''_2\text{O}_5, p\text{R}_2\text{O}$ .

D. A. L.

### Mineralogical Chemistry.

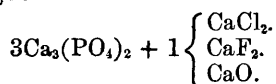
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**Brucite of Cogne, Val d'Aosta.** By FRIEDEL (*Gazzetta*, **13**, 278).  
 —This mineral gave by analysis 67.06 per cent. MgO, 1.13 FeO, 29.48 H<sub>2</sub>O, and 2.13 silica and insoluble matter, total 99.80; or deducting the silica and insoluble portion: 68.53 MgO, 1.15 FeO, and 30.13 water = 99.81, agreeing nearly with the formula MgO, H<sub>2</sub>O or Mg(OH)<sub>2</sub>, and showing that this mineral is identical with the brucites of other localities, and in particular with that of Hoboken. Like all other brucites, it is accompanied by serpentine. H. W.

**Chemical Composition of Apatites.** By J. A. VOELCKER (*Ber.*, **16**, 2460—2464).—The formula  $3\text{Ca}_3(\text{PO}_4)_2 + \begin{cases} \text{CaCl}_2 \\ \text{CaF}_2 \end{cases}$ , usually assigned to apatite, does not appear to be founded on direct determinations of all the constituents, but to have been assumed on the strength of its isomorphism with pyromorphite,  $3\text{Pb}_3(\text{PO}_4)_2 + \text{PbCl}_2$ . In par-

ticular, the fluorine seems not to have been estimated, but calculated from the excess of lime beyond that required for the phosphate and chloride.

The author has determined all the constituents in several samples of apatite, and finds that the amount of fluoride and chloride is always considerably below that required by the above formula, but that there is an excess of calcium oxide present equivalent to the deficiency in the haloid salt, and that apatite must therefore be represented by the formula—



The analyses were all made from crystals with completely smooth and sharp faces. A and B are Canadian apatites, D, Ea, Eb, and F Norwegian apatites containing no fluorine.

	A.	B.	D.	Ea.	Eb.		F.
$\text{Ca}_3\text{P}_2\text{O}_8$ .....	89.36	90.31	90.93	90.14	90.14	89.81	87.96
$\text{CaF}_2$ .....	4.54	5.03	—	—	—	—	—
$\text{CaCl}_2$ .....	0.14	0.75	2.38	1.27	1.42	1.42	3.53
$\text{CaO}$ .....	1.72	2.27	3.57	4.98	4.34	4.36	3.68
$\text{CaCO}_3$ .....	1.95	—	0.20	—	—	—	—
$\text{CaSO}_4$ .....	0.54	—	0.24	0.25	0.22	0.22	0.25
$\text{MgO}$ .....	0.19	—	—	—	—	—	—
$\text{Fe}_2\text{O}_3$ .....	0.41	0.24	0.40	1.62	1.57	1.57	0.64
$\text{Al}_2\text{O}_3$ .....	0.86	0.99	0.92	0.85	1.04	1.04	0.39
Insoluble residue	0.15	0.99	0.64	0.34	0.24	0.39	1.89
Water.....	0.04	—	0.18	} 0.44	0.34	0.27	0.14
Loss on ignition	0.25	—	0.04				

A. J. G.

**Formation of Albite in the Wet Way.** By C. FRIEDEL and E. SARASIN (*Compt. rend.*, 97, 290—294).—When solutions of sodium silicate and aluminium silicate in the proportions necessary to form albite are heated together in a strong steel tube at about  $400^\circ$ , no albite is formed, but crystals and globules of analcime separate out in considerable quantity, a certain proportion of the sodium silicate and traces of the aluminium silicate remaining in solution. If, however, the sodium silicate is added in excess to the extent indicated by this experiment, and the solution heated at about  $500^\circ$ , crystals of albite are obtained identical in chemical composition and physical properties with the natural crystals. The crystals are sometimes slender needles, sometimes shorter and thicker prisms, and some of them show the usual albite twinning. When the solution of sodium and aluminium silicates is mixed with potassium chloride, the results are somewhat contradictory. In the first experiment, no albite was formed, but crystals of quartz and a quantity of small crystals apparently belonging to the cubical system were obtained. In other experiments, however, both albite and orthoclase were formed simultaneously, but the two minerals did

not crystallise together. Albite is formed even in liquids containing four times as much potassium as sodium, and sodium chloride even in large proportion is apparently without effect on the formation of the mineral.

C. H. B.

**Rhodonite from Viù.** By V. FINO (*Gazzetta*, **13**, 277).—This rhodonite is red, but is mixed with a black substance difficult to separate, probably a product of alteration. The rhodonite has a density of 3.65, hardness 5—5.6. It melts before the blowpipe, gives a brown bead with borax; with phosphorus salt a bead which is opaque when cold, and becomes red in the reducing flame. Its analysis gave—

SiO <sub>2</sub> .	MnO.	FeO.	CaO.	Loss by ignition.	
44.31	48.77	1.53	4.44	1.25	= 100.30
44.34	48.64	1.48	4.57	1.23	= 100.16

agreeing nearly in composition with the rhodonite of S. Marcel, in which Ebelman found 46.37 SiO<sub>2</sub>, 47.38 MnO, and 5.48 CaO.

H. W.

**Artificial Production of Rhodonite and Zephroite.** By A. GORGEU (*Compt. rend.*, **97**, 320—323).—When a current of hydrogen and carbonic anhydride charged with aqueous vapour is passed over a mixture of 10 parts manganous chloride and 1 part precipitated silica fused at a cherry-red heat, the manganous chloride is partially decomposed, yielding hydrochloric acid and manganous oxide, which dissolves in the unaltered manganous chloride and is thus brought into intimate contact with the silica. The first product is a bisilicate, which is obtained in small distinct rose-coloured crystals by treating that part of the fused mass which is insoluble in water with dilute hydrochloric acid (1 : 2). If the action of the moist gas is prolonged, and the residue after being washed with water is treated with very dilute hydrochloric acid (1 : 50), grey crystals of a normal silicate are obtained. In these experiments, the aqueous vapour is the active agent, the hydrogen or carbonic anhydride simply preventing access of air and consequent formation of hausmannite. The rose-coloured crystals have the composition SiO<sub>2</sub>,MnO, and correspond in crystalline form and other properties with rhodonite; the grey crystals have the composition SiO<sub>2</sub>.2MnO, and correspond with zephroite. The presence of alkaline chlorides has no effect on the production of these compounds. In presence of the chlorides of iron, magnesium, and calcium, small quantities of these metals are taken up, but the oxygen ratio remains the same. The artificial crystals are about a degree softer than the natural crystals. Both compounds are anhydrous, and do not appreciably oxidise in dry or moist air. They melt with difficulty at a bright red heat, forming a brown enamel, and they dissolve in fused manganous chloride, and are deposited in definite crystals on cooling. The rose-coloured silicate when fused with manganous chloride in presence of aqueous vapour, is gradually converted into the neutral silicate, and the latter, when fused with manganous chloride and silica out of contact with air and moisture, is converted

into an acid silicate, insoluble in hydrochloric acid. Hydrochloric acid has little action on the rose-coloured silicate, but attacks the neutral salt even when very dilute; sulphurous acid also has no action on the first compound, but dissolves the neutral salt. Chlorine water blackens and partly dissolves the grey crystals, but has little action on the acid salt. Saturated solutions of carbonic anhydride and hydrogen sulphide respectively decompose the neutral salt, but have no action on the other. A 2·8 per cent. solution of sodium hydrogen carbonate has very little action on the rose-coloured salt at 40–60°, but partially converts the grey silicate into carbonate. Natural rhodonite behaves in exactly the same way as the artificial product, and it would appear probable from these reactions that the manganese carbonate, sulphide, and peroxide found in mineral veins have been formed by the alteration of tephroïte rather than by that of the much more stable rhodonite.

C. H. B.

**Meteoric Dust and Analysis of the Soil of Sahara.** By TACCHINI (*Gazzetta*, 13, 327).—An investigation as to the origin of the rains of sand and meteoric dust which fall in Italy, and especially in Sicily, shows that the sand comes from Africa, being raised by cyclones, and carried into Sicily and Italy by the strong south-east and south-west currents. Tacchini and Macagno are comparing these powders with the soil from the Desert of Sahara.

C. E. G.

**Analysis of the Brine-Spring of Stoke Prior, Worcestershire.** By A. B. GRIFFITHS (*Chem. News*, 48, 207).—This deposit of rock-salt is in the lias; the water is pumped from a depth of over 300 feet. The following are the results of analyses recently made by the author, which are compared with results obtained by Northcote in 1854:—

	Northcote (1854.) Per cent.	Griffiths (1883.)	
		I. Per cent.	II. Per cent.
Soda .....	13·7779	13·7741	13·7752
Lime .....	0·1075	0·1092	0·1085
Magnesia .....	0·0165	0·0159	0·0173
Ferric oxide .....	trace	trace	trace
Chlorine .....	15·4697	15·4620	15·4683
Phosphoric acid ....	trace	trace	trace
Silicic acid .....	trace	trace	trace
Lithium .....	—	trace	trace
Bromine .....	trace	trace	trace
Potash .....	trace	trace	trace
Sulphuric acid .....	0·4888	0·4890	0·4892

It contains 25·49 per cent. sodium chloride, the brine is therefore a saturated solution; the sp. gr. is 1·2049 at 24°.

D. A. L.



## Organic Chemistry.

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**Galician Petroleum.** By B. LACHOWICZ (*Annalen*, **220**, 188—206).—The volatile portion of the petroleum from Boryslaw, in Galicia, boiling between 30° and 125°, contains the following hydrocarbons:—(1) Isopentane boiling at 30°, which yields a chloride boiling at 100° (sp. gr. 0·8703 at 20°); (2) normal pentane boiling at 37° (sp. gr. 0·6267 at 14°), yielding two chlorides boiling at 106° and 104°; (3) a hexane boiling at 60°; (4) hexane boiling at 70° (sp. gr. 0·6985 at 14°); (5) heptane boiling at 99°; (6) nonane boiling at 148°; and (7) decane boiling at 152°, and a decane boiling at 162—163° (sp. gr. 0·7324 at 20°); also benzene, toluene, xylene, and mesitylene. The petroleum does not contain any olefines. The author is of opinion that olefines do not occur ready formed in petroleum, but that they are produced in the process of distillation.

The relatively high sp. gr. of certain portions of the distillate of the petroleum, from which the hydrocarbons of the benzene series have been removed, leads the author to infer the presence of the hydrides of the aromatic hydrocarbons, *e.g.*, hexahydrotoluene and hexahydro-isoxylene.  
W. C. W.

**Some Paraffins and their Derivatives.** By B. LACHOWICZ (*Annalen*, **220**, 168—188).—*Diamyl*,  $C_{10}H_{22}$ , prepared by the action of sodium on amyl bromide from commercial amyl alcohol, boils at 157·1°, and has the sp. gr. 0·72156 at 22°. It is a tasteless liquid, having a faint odour. It is soluble in 12 parts of acetic acid at the ordinary temperature, and is miscible with alcohol, ether, benzene, and chloroform in all proportions; it is not attacked by sulphuric or nitric acid. The hydrocarbon ignites at 53°. No bromide could be isolated by the action of bromine on diamyl, as the product splits up into decylene and hydrobromic acid on distillation. Decylene (boiling at 161·5°) has an aromatic odour.

Normal decane, obtained by the action of sodium on a mixture of octyl and ethyl bromides diluted with benzene, is tasteless, and almost inodorous. It boils at 169·5°, and ignites at 55°. Its sp. gr. at 18° is 0·73097. Dioctyl (melting at 19—20°) is obtained as a bye-product. Secondary octyl bromide (sp. gr. 1·0989 at 22°), boils at 188°, with slight decomposition. Octylene boils at 122·4°.

When sodium acts on a mixture of ethyl bromide and secondary octyl bromide, dioctyl and butane are formed, but decane is not produced. Dioctyl is a thick colourless liquid, boiling at 263° (sp. gr. 0·80011 at 11°). The paraffins are almost devoid of smell.

W. C. W.

**Butylene and its Derivatives.** By E. PUCHOT (*Ann. Chim. Phys.* [5], **28**, 507—569).—Butylene is most conveniently prepared by warming a mixture of fermentation butyl alcohol ( $2\frac{1}{2}$  parts), sulphuric acid ( $2\frac{1}{2}$  parts), plaster of Paris (4 parts), and potassium sulphate

(1 part). The gas is passed through two flasks containing milk of lime or soda; it is then dried over quicklime, and condensed by a freezing mixture. At the ordinary temperature, water absorbs one-tenth its volume of the gas, alcohol 36 vols., and glacial acetic acid, 62 vols. Liquid butylene boils at  $-4^{\circ}$ . Its sp. gr. at  $-14.2^{\circ}$  is 0.639. Butyl butyrate and isobutylene are obtained in small quantities as by-products in the preparation of butylene. They are also formed by the action of phosphorus pentachloride on butyl alcohol, and butyl butyrate is produced on heating butyl alcohol with phosphoric anhydride. Butylene is absorbed by sulphuric acid, yielding isobutylene boiling at  $180^{\circ}$ , and a mixture of isomeric bodies boiling between  $172^{\circ}$  and  $244^{\circ}$ . Butylene unites with bromine to form the dibromide  $C_4H_8Br_2$ , a colourless liquid boiling at  $153^{\circ}$  (sp. gr. at  $0^{\circ} = 1.8053$ ); with hydriodic acid it yields an iodide which boils with decomposition at  $100-25^{\circ}$ . Cold concentrated hydrochloric acid absorbs butylene with formation of the tertiary chloride boiling at  $55^{\circ}$  (sp. gr. 0.8658 at  $0^{\circ}$ ). In diffused daylight chlorine unites with butylene to form the dichloride  $C_4H_8Cl_2$ , boiling at  $129^{\circ}$ . The product of the action of alcoholic potash on this chloride contains oxygen. At the ordinary temperature in direct sunlight, chlorine replaces 4 atoms of hydrogen in the chloride, yielding the compound  $C_4H_4Cl_6$ . At a higher temperature, chlorine expels two more atoms of hydrogen and  $C_4H_2Cl_6$  is formed. The former compound is decomposed by alcoholic potash; 4 mols. of hydrochloric acid being eliminated, and  $C_4Cl_2$  produced: it is an unstable liquid, which appears to boil above  $200^{\circ}$ . Alcoholic potash decomposes the chloride  $C_4H_2Cl_6$ , yielding a compound having the composition  $(C_4Cl_4)_n$ .  
W. C. W.

**Some Reactions of Tertiary Alcoholic Iodides.** By K. BAUER (*Annalen*, **220**, 158—168).—Tertiary pentyl iodide is decomposed by water into hydriodic acid and ethyl dimethyl carbinol. It is also decomposed by methyl alcohol at  $100^{\circ}$ , yielding methyl iodide and tertiary amyl alcohol. Under similar treatment tertiary butyl iodide yields methyl iodide and trimethyl carbinol. On heating a mixture of methyl acetate and tertiary butyl or amyl alcohol for several hours, methyl iodide, acetic acid, and butylene or amylene are produced.  
W. C. W.

**Menthyl Chloride.** By G. ARTH (*Compt. rend.*, **97**, 323—324).—When an ethereal solution of menthene is treated with hydrochloric acid gas, or when menthene and a concentrated solution of hydrochloric acid are heated together in sealed tubes at  $120^{\circ}$ , menthene hydrochloride,  $C_{10}H_{18}HCl$ , is obtained. It is an oily liquid, which burns with a green-edged flame, and cannot be distilled without decomposition. When boiled with water, it yields hydrochloric acid and menthene, and when heated with silver acetate in a closed vessel, it yields acetic acid, silver chloride, and menthene, but no menthyl acetate. This compound therefore agrees in its properties with the menthyl chloride obtained by Oppenheim by the action of concentrated hydrochloric acid on menthol in a closed vessel, and the author considers that the two compounds are identical, just as camphene hydrochloride and the chloride obtained from borneol are identical. These last two compounds, how-

ever, appear to be true hydrochloric ethers, whilst the derivatives of menthol have no analogy to the hydrochlorides of terebenthene.

The menthene used by the author was dextrogyrate, unlike that of Walter, Oppenheim, and Moriya, which was inactive. C. H. B.

**Silver Nitrocyanide.** By C. L. BLOXAM (*Chem. News*, 48, 154).—The author has examined the crystalline compound obtained by dissolving pure silver cyanide in a nearly saturated boiling solution of silver nitrate. It is anhydrous, and is decomposed by water into silver cyanide and nitrate. Analysis gives 68.09 per cent. total silver, determined in nitric acid solution of the compound; 22.97 per cent. silver as cyanide, determined in residue from decomposition with water; 45.64 per cent. silver as nitrate, determined in aqueous extract. Its constitution is therefore  $\text{AgCy}_2\cdot 2\text{AgNO}_3$ , and not  $\text{AgNO}_3\cdot 2\text{AgCy}$ , as is generally supposed. D. A. L.

**Reaction between Mercuric Cyanide and Silver Nitrate in Presence of Ammonia.** By C. L. BLOXAM (*Chem. News*, 48, 161).—Wöhler obtained a salt having the formula  $\text{AgNO}_3\cdot \text{HgCy}_2 + 2\text{Aq}$ , from which, according to *Gmelin's Handbook*, alkalis throw down silver cyanide, a reaction incompatible with the above formula. The author has investigated the subject, and his results form the substance of this paper.

When neutral solutions of mercuric cyanide and silver nitrate are mixed together, the mixture becomes acid, indicating the formation of mercuric nitrate, whilst it deposits a crystalline double salt. The same salt is formed when precipitated silver cyanide is dissolved in a solution of mercuric nitrate. The aqueous solution of the salt is precipitated by ammonia and by hydrocyanic acid, which causes the separation of silver cyanide, indicating the presence of silver nitrate in the salt.

If mercuric cyanide in solution is added by degrees to an ammoniacal solution of silver nitrate, a white, opaque and silky crystalline precipitate separates. The two precipitates have the same composition, and the numbers from analysis, after corrections have been made for impurities, agree with those required by the formula  $2\text{HgO}, \text{HgCy}_2, 7\text{AgCy}$  :—

	Ag.	Hg.	Cy.
Calculated (for formula) ..	46.60	36.99	14.42
Found .....	46.43	37.03	14.29

The impurities found were 0.32 per cent. of ammonia and 2.11 per cent. nitric acid. The silver was determined as chloride, the mercury as sulphide, and the cyanogen by converting it into ammonium thiocyanate, and subsequent precipitation with silver nitrate. Both precipitates are anhydrous and explode when heated, the opaque one more violently than the crystalline. The filtrate from these precipitates deposits silver cyanide, and the filtrate from this contains a small quantity of silver and much mercury and cyanogen.

The author is therefore of opinion that in the above experiments the mercuric cyanide and silver nitrate are converted, at least par-

tially, into silver cyanide and mercuric nitrate, and the precipitate formed in the presence of ammonia is composed of silver cyanide and mercuric oxycyanide.

D. A. L.

**Influence of Asymmetrical Carbon-atoms on the Ethanes Derived from Active Amyl Alcohol.** By F. JUST (*Annalen*, **220**, 146—157).—In order to observe the influence of asymmetrical carbon-atoms on the optical activity of organic compounds, and to test the accuracy of Le Bel's hypothesis (*Bull. Soc. Chim.* [2], **22**, 337) the author has examined a series of the derivatives of active amyl alcohol. The amyl alcohol was prepared from fusel oil by Le Bel's process. Repeated attempts to obtain the methylamyl described by Le Bel (*ibid.* [2], **25**, 545) proved unsuccessful, but the following compounds were investigated. *Isopentane*, boiling at 30°, prepared by the action of zinc and hydrochloric acid on an alcoholic solution of active amyl iodide; *methylethylpropylmethane*, boiling at 91°, from amyl and ethyl iodides, and *diamyl* which yielded the following results:—

	Sp. gr.	[ $\alpha$ ].
Amyl alcohol, $C_2H_5.CHMe.CH_2.OH$ .....	—	—2·82
Amyl iodide, $C_2H_5.CHMe.CH_2I$ .....	1·5425 at 16°	+2·43
Ethyl dimethylmethane, $C_2H_5.CHMe_2$ .....	0·6375 at 13	0
Methylethylpropyl- methane .....	} $C_2H_5.CHMe.CH_2.CH_2Me..$ 0·6895 at 20	+3·93
Active diamyl, $C_2H_5.CHMe.CH_2.CH_2.CHMe.C_2H_5$		
	0·7463 at 22	+8·69

These results confirm the accuracy of Le Bel's hypothesis.

W. C. W.

**$\beta$ -Butyl Glycol.** By A. WURTZ (*Compt. rend.*, **97**, 473—475).—The action of sodium-amalgam on a cold dilute slightly acid solution of aldol yields butyl glycol, which forms a thick perfectly colourless liquid boiling at 207—208° under a pressure of 769 mm., and soluble in all proportions in water, alcohol, and ether; sp. gr. at 0° = 1·0259. It is violently attacked by phosphorus pentachloride, with formation of a small quantity of a chloride boiling at 130—135°, and another product which cannot be distilled, but which contains both chlorine and phosphorus. Acetic chloride also reacts violently with butyl glycol, forming hydrochloric acid and an acetin which cannot be purified from chlorine even by distillation with silver acetate. The same acetin is easily obtained by heating the glycol at 100° in sealed tubes for several days with 6 or 8 times its weight of acetic anhydride. It forms a colourless neutral liquid, insoluble in water, with a feeble acetic odour; sp. gr. at 0° = 1·055. It has the composition  $C_4H_9(ACO)_2$ . When the butyl glycol is heated for some time with a large excess of highly concentrated hydriodic acid it yields butylene di-iodide,  $C_4H_8I_2$ , probably  $CHMeI.CH_2CH_2I$ ; sp. gr. at 0° = 2·291.

That fraction of the crude butyl glycol which boils at 220—250° under ordinary pressure, contains a substance which boils at 160—165° under a pressure of 15 mm. It has the same composition as dialdanic alcohol,  $C_{14}H_{18}O_3$ , and is probably an isomeride of that body. It yields an acetin.

C. H. B.

**Fermentation of Glycerol with the Bacteria from Ammonium Tartrate.** By A. VIGNA (*Gazzetta*, **13**, 293—296; *Ber.*, **16**, 1438).—The glycerol (2,200 grams) mixed with a solution of potassium phosphate (22 grams) and ammonium tartrate (44 grams), is diluted with water (40 litres), and a small portion of liquid containing the bacteria of ammonium tartrate added; this is easily obtained by adding to a solution of ammonium tartrate a small quantity of the salts necessary to nourish the bacteria, and exposing it to the air until they have developed. The glycerol mixture is allowed to ferment for two months at a temperature of 20—25°, adding calcium carbonate from time to time to neutralise the paraffin acids as they are formed: hydrogen and carbonic anhydride are evolved during the whole time that the fermentation is going on; when gas is no longer given off the liquid is distilled with excess of calcium carbonate; ethylic alcohol (72 grams), normal butylic alcohol (196 grams), and an insignificant quantity of the higher alcohols pass over with the aqueous vapour. The author has not as yet examined the residuum containing the calcium salts. As the yield of normal butyl alcohol is 9 per cent. of the glycerol employed, it seems to be the most convenient process for preparing that compound. C. E. G.

**Electrolysis of Glycerol with Electrodes of Carbon and Platinum.** By A. BARTOLI and G. PAPASOGLI (*Gazzetta*, **13**, 287—293).—The authors have already published on this subject (*Abstr.*, 1882, 406).

*Electrolysis with Gas-carbon Electrodes.*—The glycerol diluted with an equal bulk of dilute sulphuric acid (1 : 5), was electrolysed, using six Bunsen's elements which were renewed every five days; the negative electrode was of platinum, and the positive of gas-carbon; hydrogen in abundance was evolved at the negative pole, and but very little gas at the positive pole, which was rapidly disintegrated, being reduced to one-third of its weight after the action had continued for a month. An abundant black deposit of carbon mixed with mellogen formed at the bottom of the voltmeter; the liquid became dark, and there was an intense, suffocating odour of acraldehyde.

The liquid, filtered from the black deposit and neutralised with barium carbonate, yielded a nearly colourless solution; on distilling this, water passed over, together with trioxymethylene which is left in the crystalline state on evaporating the distillate over sulphuric acid (Rénard, *Abstr.*, 1880, 25). It melts at 155°, is but sparingly soluble in water, insoluble in alcohol, and reduces Fehling's solution and nitrate of silver. When hydrogen sulphide is passed into its solution at 60°, a white precipitate of methylene oxysulphide,  $(C_3H_6S_2O)_2 \cdot H_2O$ , is obtained: this has a marked alliaceous odour, and melts at 80°. If the aqueous solution of trioxymethylene is evaporated on the water-bath, taking care always to keep it strongly alkaline with ammonia, a substance is obtained melting at 120—125°, and having all the properties of Butlerow's hexamethylenamine,  $C_6H_{12}N_4$ .

The solution of barium salts remaining in the retort was carefully examined and found to contain glyceric acid and a small quantity of a saccharine substance, but no benzenecarboxylic acids; much undecomposed glycerol was also present.

*Electrolysis with Graphite Electrodes.*—The electrolysis took place in much the same way as with the carbon electrodes, only that the solution remained colourless, and the graphite (positive) electrode was but very little disintegrated, the small quantity of black deposit formed consisting of a mixture of unaltered graphite with graphitic oxide.

The solution, when neutralised with barium carbonate and distilled, yielded trioxymethylene, and the residue in the retort was found to contain, besides glycerol, formic acid and a substance having many of the characters of a glucose, but incapable of undergoing fermentation; with ammoniacal lead acetate this new compound yields a white precipitate insoluble in water. The glucose solidifies over sulphuric acid, but is not crystallisable; it is soluble in alcohol, and easily reduces Fehling's solution and ammoniacal silver nitrate.

*Electrolysis with Platinum Electrodes.*—When both the electrodes are of platinum, gas is evolved in abundance at both poles; there is a powerful odour of acraldehyde, and the liquid remains colourless. The solution when treated in the way previously described was found to contain formic and glyceric acids and a minute quantity of a substance resembling a glucose.

C. E. G.

**Maltose.** By A. HERZFELD (*Annalen*, **220**, 206—224).—The rotatory power of a 5 per cent. solution of pure maltose was found to be  $[\alpha]_D = 139^\circ$ , which agrees closely with Soxhlet's results  $[\alpha]_D = 139.3^\circ$ , and differs considerably from that found by O'Sullivan,  $[\alpha]_D = 149.5^\circ$ . Maltose forms the following compounds with sodium and calcium,  $C_{12}H_{21}NaO_{11}$  and  $C_{12}H_{20}CaO_{11} + H_2O$ , and analogous compounds with barium and strontium.

The octacetic derivative,  $C_{12}H_{14}O_{11}Ac_8$ , crystallises in thin prisms which belong to the mono- or tri-clinic system. The crystals melt with decomposition at  $150$ — $155^\circ$ . They are soluble in ether, warm alcohol, benzene, and acetic acid. For the solution in benzene  $[\alpha]_D = 81.18^\circ$ .

The reducing action of maltose on Fehling's solution is equal to about two-thirds of that of glucose, but if the filtrate from the cuprous oxide is acidified with hydrochloric acid the solution slowly acquires the power of reducing a further quantity of Fehling's solutions equal to about half the volume originally reduced. In this respect maltose resembles lactose. A second point of analogy is that neither of these sugars form double salts with borax, or with potassium or sodium chlorides or bromides.

Maltose is not a simple anhydride of glucose; its molecular weight must be at least 3 times as great as that of diglucose.

W. C. W.

**Saccharin.** By C. SCHEIBLER (*Ber.*, **16**, 24—34).—In the preparation of saccharin by the action of the alkaline-earths on the glucoses, the author has observed that a vigorous absorption of oxygen from the air always occurs. He is working at this subject and also at the action of aqueous ammonia on the glucoses.

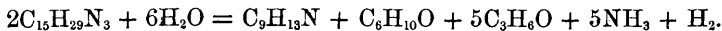
A. J. G.

**Diethyl Methylene Ether.** By L. PRATESI (*Gazzetta*, **13**, 313—315).—On distilling a mixture of paraformaldehyde (trioxymethylene) with ethyl alcohol and sulphuric acid—continuing the distillation

until it becomes turbid on the addition of water,—a product is obtained which, when treated with water and calcium chloride, yields impure diethyl methylene ether,  $\text{CH}_2(\text{OEt})_2$ . It may be purified by digesting it with potash, first in a flask furnished with a reflux condenser, and then with fresh potash in a sealed tube heated at  $100^\circ$ . It boils at  $87\text{--}88^\circ$ , has a sp. gr. of 0.8504 at  $0^\circ$ , and a vapour-density of 102 referred to hydrogen,  $\text{C}_3\text{H}_{12}\text{O}_2$  requiring 104. It is less soluble in warm water than in cold, requiring 11 vols. of water at  $18^\circ$  for that purpose, and 15 vols. at  $30^\circ$ .

The boiling point and solubility of the substance show that it is isomeric with Wurtz's methylacetyl, so that there can be no doubt the formula  $\text{C}_2\text{H}_4(\text{OEt}).\text{OMe}$ , assigned by Wurtz to the compound obtained by the action of sulphuric acid and manganese dioxide on a mixture of ethyl and methyl alcohols, is correct. C. E. G.

**Action of Ammonia on Propaldehyde.** By A. WAAGE (*Monatsh. Chem.*, 4, 708—732).—This paper gives a detailed account of experiments, a preliminary notice of which has already been published (Abstr., 1883, p. 39). These experiments confirm the formation of parvoline,  $\text{C}_9\text{H}_{13}\text{N}$ , from the crystalline compound  $\text{C}_{15}\text{H}_{25}\text{N}_3$  produced by the action of carbonic acid on propaldehyde-ammonia,  $\text{C}_3\text{H}_5\text{O.NH}_3$  or  $\text{CH}_2\text{Me.CH}(\text{NH}_2)(\text{OH})$ , or from its mother-liquor or the crude product containing the two. When this crystalline product is heated with dilute hydrochloric acid, propaldehyde and methylethylacetaldehyde,  $\text{C}_6\text{H}_{10}\text{O}$ , distil over, and the residue distilled with potash yields parvoline, together with a dark resinous residue:



Parvoline thus obtained is a mobile, colourless, strongly refracting liquid, boiling at  $198\text{--}200^\circ$ , lighter than water, having a very strong aromatic odour like that of the other pyridine-bases, and an extremely bitter taste. It is not very soluble in water, but dissolves readily in alcohol and ether; forms white fumes with hydrochloric acid, and colours pine-wood yellow. With *picric acid*, it forms a compound containing molecular proportions of its two constituents. This compound forms crystalline laminae having the colour of picric acid, more soluble in alcohol than in water, melting at  $149^\circ$ . With *tannin solution*, parvoline forms a white flocculent precipitate, easily soluble in alcohol; with phosphotungstic acid it forms a faint bluish-white body, which increases on addition of hydrochloric acid and is insoluble in alcohol; with *potassio-mercuric iodide*, a yellowish-white precipitate, easily soluble in alcohol and in hydrochloric acid. Iodised solution of potassium iodide forms with it a brown flocculent precipitate soluble with violet colour in carbon sulphide. Potassio-bismuthous iodide forms a dark brown precipitate soluble in hydrochloric acid, and coloured yellow by alcohol. Parvoline aurochloride crystallises in deliquescent yellow needles.

The parvoline formed as above agrees with that which is obtained from bituminous shale in all its properties except the boiling point, which the author finds to be  $198\text{--}200^\circ$ , whereas shale parvoline boils at  $188^\circ$ . The lower boiling point of the latter is probably due to the admixture of lower homologues.

The decomposition of the compound  $C_{15}H_{23}N_3$  by hydrochloric acid yields also a small quantity of a lower base of the series, viz.,  $C_6H_5N$  (composition determined by analysis of platinochloride), which distils for the most part at  $160^\circ$ , has a more pungent odour than parvoline, and appears to be identical with picoline.

*Oxidation of Parvoline.*—This base oxidised with potassium permanganate is converted into a pyridine-dicarboxylic acid,  $C_7H_5NO_4 = C_5H_3N(COOH)_2$ , which crystallises in crusts of chalky microscopic needles melting at  $219^\circ$ . It gives a red coloration with ferrous sulphate; with lead acetate after a while a white precipitate insoluble in excess; with silver nitrate a white flocculent precipitate, easily soluble in ammonia and in nitric acid; blue-green with cupric acetate. Its *cadmium salt* is obtained by precipitation, as a white crystalline body,  $C_7H_3NO_4Cd, 4H_2O$ , which gives off half its water on prolonged standing over sulphuric acid, or when heated to  $140^\circ$ . In most of these characters the acid in question agrees with lutidic acid (*Monatsh. Chem.*, **1**, 20); the latter however and its copper salt are described as containing crystal-water, whereas the pyridine-dicarboxylic acid described above and its copper salt are anhydrous; lutidic acid is also described as more soluble in water than Waage's acid. The calcium salt of the acid heated in a tube with excess of quicklime yielded a distillate of pyridine. H. W.

**Tobacco Fat.** By R. KISSLING (*Ber.*, **16**, 2432—2434).—The vegetable wax occurring in tobacco, and usually termed "tobacco fat," has not previously been obtained in a state of purity. To prepare it, tobacco is extracted with ether, the extract, after the removal of the greater part of the ether, mixed with alcohol and the precipitated wax purified by repeated crystallisation from hot alcohol. The wax then forms a snow-white mass of satiny lustre, melts at  $63^\circ$ , and on analysis gave numbers agreeing with the formula  $C_{70}H_{140}O_2$ , but after removal of a small quantity of a substance insoluble in cold ether, the results agreed better with  $C_{60}H_{120}O_2$  (mellissyl-mellisate).

Kentucky tobacco yielded 0.18 per cent. of wax.

In the course of some investigations on the constituents of tobacco-smoke, a wax-like body was obtained, similar in appearance to tobacco-wax, melting at  $64.5^\circ$ , but appearing, from its analysis, to be a hydrocarbon containing C 84.7—85.5 per cent., and H 14.63—15.16 per cent.

A. J. G.

**An Isomeride of Laurene.** By A. RENARD (*Compt. rend.*, **97**, 328—330).—When that portion of crude rosin-oil which boils between  $180^\circ$  and  $200^\circ$  is treated repeatedly with sulphuric acid and carefully distilled, it yields a light oil which boils at  $193$ — $195^\circ$ , and is not attacked by ordinary sulphuric acid. This liquid has the composition  $C_{11}H_{16}$ ; vapour-density, 5.37; sp. gr. at  $19^\circ = 0.8588$ . It is an isomeride of laurene. It dissolves in fuming nitric acid with development of heat and evolution of nitrogen oxides, forming a heavy oily orange-coloured mononitro-derivative,  $C_{11}H_{15}NO_2$ . The hydrocarbon is only slightly attacked by ordinary nitric acid in the cold, but yields isophthalic acid when boiled with it. It is, therefore, metaethyl-propylbenzene,  $C_6H_4EtPr$  [1 : 3]. On treating it with fuming sul-



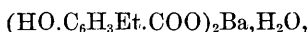
phuric acid, a sulphonic acid is formed. The barium salt is somewhat soluble in boiling water, but only very slightly soluble in cold water. It forms brilliant white crystalline plates which, when dried at  $100^{\circ}$ , have the composition  $(C_{11}H_{15}SO_3)_2Ba + H_2O$ , but become anhydrous at  $175^{\circ}$ .

The metaethylpropylbenzene contains a small quantity of a hydrocarbon which is not attacked by fuming sulphuric acid or by ordinary nitric acid. It is in all probability one of the higher members of the  $C_nH_{2n-6}H_6$  series.

C. H. B.

**Chemical Nature of Phlorol.** By V. OLIVERI (*Gazzetta*, **13**, 263—269).—When barium phloretate is distilled over an open fire with lime and powdered glass, part of it is resolved into phlorol,  $C_8H_{10}O$ , and carbonic acid:  $(C_8H_9O_3)_2Ba + CaH_2O_2 = 2C_8H_{10}O + CO_3Ba + CO_3Ca$ , while a portion of the phlorol undergoes further decomposition into ethylene and ordinary phenol:  $C_8H_{10}O = C_2H_4 + C_6H_6O$ . The phlorol thus obtained is a colourless strongly refractive liquid, having the characteristic odour of the phenols, boiling at  $210$ — $212^{\circ}$ , soluble in alcohol and ether, slightly soluble in water. Its aqueous solution gives a faint green coloration with ferric salts. Its potassium salt is easily decomposed by carbonic acid. The *methyl ether*,  $C_8H_{12}O = C_6H_4Et.MeO$ , prepared by digesting molecular proportions of phlorol and potassium hydroxide dissolved in anhydrous methyl alcohol, is a heavy strongly refracting oil having a pleasant etheric odour, boiling at  $185^{\circ}$ , not oxidised by potassium permanganate.

*Phlorolcarboxylic acid*,  $C_8H_{10}O_3 = HO.C_6H_3Et.COOH$ , prepared by heating phlorol with sodium and carbonic anhydride, crystallises in slender silky colourless needles, slightly soluble in cold water, very soluble in alcohol and in ether, melting at  $112^{\circ}$ . Its aqueous solution is coloured violet by ferric chloride. Its *barium salt*,



crystallises in small scales. By fusing phlorol with potassium hydroxide, two acids are obtained, viz., salicylic acid melting at  $156$ — $158^{\circ}$ , and a small quantity of metahydroxybenzoic acid, at  $190$ — $195^{\circ}$ .

The phlorol prepared as above is identical with the *ortho*-ethylphenol,  $C_6H_4Et.OH$ , which Suida and Plhon obtained by the action of nitrous acid on amidethylbenzene (*Abstr.*, 1881, 268), and Beilstein and Kuhlberg by fusing potassium ethylbenzenesulphonate with potassium hydroxide (*Annalen*, **156**, 211), the products formed in these several processes agreeing in boiling point, in their behaviour with fused potash, and with bromine-water, and in yielding carboxylic acids exhibiting similar properties.

H. W.

**Nitroresorcinols.** By G. SCHIAPARELLI and M. ABELLI (*Gazzetta*, **13**, 257).—*Mononitrodibenzoresorcinol*,  $C_6H_3(NO_2)(OBz)_2$ , obtained by heating dibenzoresorcinol (m. p.  $117^{\circ}$ ) with a mixture of sulphuric and nitric acids, crystallises in stellate groups of needles melting at  $107^{\circ}$ , and is resolved by saponification into benzoic acid and mononitroresorcinol melting at  $115^{\circ}$ .

*Trinitrodibenzoresorcinol*,  $C_6H(NO_2)_3(OBz)_2$ , is formed on dissolving dibenzoresorcinol in cold strong nitric acid (sp. gr. 1.5), and separates

on addition of water, as a faintly yellowish solid substance which, after crystallisation from methyl alcohol, melts at  $123^{\circ}$ . By saponification with alcoholic potash, it is resolved into metanitrobenzoic acid and nitroresorcinol melting at  $115^{\circ}$ , ethyl metanitrobenzoate melting at  $43^{\circ}$  being formed at the same time. The separation of the *m*-nitrobenzoic acid and nitroresorcinol was effected by the different solubilities of their copper-salts.

On dissolving diacetylresorcinol in well cooled nitric acid of sp. gr. 1.45 and adding water, a white or slightly yellowish substance separates, consisting of a mixture of dinitroresorcinol and styphnic acid, melting at  $175^{\circ}$ . The dinitroresorcinol separated from this mixture by fractional crystallisation, melts at  $214.5^{\circ}$ . H. W.

**Arbutin.** By J. HABERMANN (*Monatsh. Chem.*, **4**, 753—786).—This paper gives a detailed description of a large number of experiments on the composition of arbutin and its behaviour at high temperatures, tending to establish the correctness of the formula  $C_{26}H_{34}O_{14}$ , deduced by Hlasiwetz and Habermann for arbutin, from the occurrence of methylquinol,  $C_7H_8O_2$ , as a product of its decomposition (*Ber.*, **14**, 302), in opposition to the view put forward by H. Schiff (*Gazzetta*, **11**, 99; and *Abstr.*, 1881, 610) and Michael (*Ber.*, **14**, 2097; and *Abstr.*, 1882, 174) that two different arbutins occur in nature, viz., arbutin,  $C_{12}H_{16}O_7$ , and methylarbutin,  $C_{13}H_{18}O_7$ . H. W.

**Hydroxybromotoluquinone.** By G. SPICA and O. MAGNANIMI (*Gazzetta*, **13**, 312—313).—A paper by Spica and Canzoneri on some brominated derivatives of toluquinone has been already published (*Abstr.*, 1883, 330), in which it is stated that the action of potassium hydroxide on tribromotoluquinone gave rise to resinous products from which nothing could be obtained in a state fit for analysis. The authors now find that on treating the tribromoquinone with a 5 per cent. solution of potassium hydroxide in the cold, it dissolves, and on acidifying with hydrochloric acid a reddish flocculent precipitate is obtained. This is somewhat difficult to purify, but by repeated treatment with cold benzene the impurities are dissolved, and a reddish-white substance is left; this may be purified by recrystallisation, first from dilute alcohol, and then by dissolving it in absolute alcohol and allowing it to crystallise by spontaneous evaporation. It forms pale rose-coloured crystals of the composition  $C_8HMeBr_2(OH) : O_2$ , melting at  $196$ — $197^{\circ}$ . The yield is very small, being only about 5 per cent. of the tribromotoluquinone employed. When submitted to the reducing action of sodium amalgam it does not yield a hydroxytoluquinol, but the action goes further, and cresol is formed. From want of material the authors have not as yet been able to ascertain which cresol this is. C. E. G.

**Electrolysis of Pyrogallol.** By E. ROTONDI (*Gazzetta*, **13**, 279).—By electrolysing solutions of pyrogallol acidulated with sulphuric acid, the author has obtained, at the positive pole, mixed with other products, a crystalline substance, which after recrystallisation exhibits all the properties of purpurogallin. From his electrolytic researches he is in-

clined to think that purpurogallin is not a direct product of the oxidation of pyrogallol, but is derived from an intermediate compound.

H. W.

**Pyrocoll.** By G. L. CIAMICIAN and P. SILBER (*Gazzetta*, 13, 320—322).—In a paper by Ciamician and Danesi (Abstr., 1882, 875), they described a compound of the formula  $C_5Cl_7NO$ , obtained by the action of phosphorus pentachloride at  $250^\circ$  on perchloropyrocoll, which evolved ammonia in abundance when boiled with potassium hydroxide solution. This compound is decomposed when heated with water at  $130^\circ$  into ammonia, carbonic and hydrochloric acids, and an acid free from nitrogen, which may be extracted from the solution by means of ether. It melts at  $85$ – $86^\circ$ , and has all the properties of the  $\alpha$ -dichloroacrylic acid obtained from mucochloric acid by Bennet and Hill (Abstr., 1879, 616). The barium and silver salts also correspond with those described by these chemists.

It would seem, therefore, that the decomposition of the compound  $C_5H_7NO$  takes place in the manner represented by the equation  $C_5H_7NO + 5H_2O = C_3Cl_2H_2O + 5HCl + NH_3 + 2CO_2$ .

C. E. G.

**Synthesis of Acetylphenylparacoumaric and Phenylparacoumaric Acids.** By A. OGLIALORO (*Gazzetta*, 13, 173).—The first of these acids is formed on heating parahydroxybenzoic acid aldehyde with acetic anhydride and sodium alphasoluate; the second by boiling the first with baryta-water. Acetylphenylparacoumaric acid melts at  $170^\circ$ , phenylparacoumaric acid at  $219^\circ$ .

H. W.

**Synthesis of Phenylmelilotic Acid.** By S. SARDO (*Gazzetta*, 13, 273).—This acid, discovered by Ogialoro (*Gazzetta*, 9, 428; and Abstr., 1880, 164), is formed by the action of sodium amalgam on phenylcoumarin dissolved in dilute alcohol. On decanting the resulting alkaline solution, filtering, and acidifying with hydrochloric acid, a viscid substance separates, from which, by fractional extraction with ether, evaporation, treatment of the residue with water containing a little alcohol, and fractional crystallisation, *phenylmelilotic acid*,  $C_{15}H_{11}O_3 = C_9H_5PhO_3$ , is obtained in small prisms, melting at  $120^\circ$ , slightly soluble in cold, more readily in boiling water, also in ether, alcohol, benzene, and chloroform. Its *silver salt*,  $C_{15}H_{13}O_3Ag$ , obtained by precipitation, is white, alterable by light, slightly soluble in cold, somewhat more freely in boiling water, and crystallisable.

H. W.

**Electrolysis of Solutions of Ammonia and Ammoniacal Salts with Carbon Electrodes.** By A. BARTOLI and G. PAPASOGLI (*Gazzetta*, 13, 281—286).

*Electrolysis of Solutions of Ammonia with Electrodes of Gas-carbon or Wood-charcoal.*—Pure ammonia solution is electrolysed with difficulty, requiring a powerful pile, but if it is mixed with an alkaline salt the liquid conducts the current and is decomposed. The authors employed a saturated aqueous solution of ammonia mixed with half its volume of a solution of pure sodium chloride and a pile of four to six Bunsens, which was allowed to act for periods varying from a week to two months, the battery charges being renewed every

three or four days. The carbon used for the electrodes was purified by heating it to a very high temperature in a current of chlorine. The evolution of gas from the negative electrode was considerable, although but little was given off from the positive: the latter was strongly acted on, and a black powder was deposited at the bottom of the voltameter, whilst the supernatant liquid was almost colourless. The solution evolved abundance of carbonic anhydride when neutralised with hydrochloric acid, and the addition of barium chloride then produced a precipitate from which mellic, pyromellic, and hydromellic acids were isolated and recognised; the filtrate from the mixed barium salts contained hydroxyromellic acid.

The black precipitate at the bottom of the voltameter, after being washed free from ammonia, was boiled for a long time with soda solution, filtered, and the black filtrate precipitated with hydrochloric acid in excess: this precipitate is insoluble in water or acids. It is black, uncrystallisable, neither melts nor volatilises, and contains carbon, hydrogen, oxygen, and nitrogen. Like mellogen, it yields benzenecarboxylic acids when treated with oxidising agents, but differs from it in containing nitrogen.

*Electrolysis of Ammoniacal Salts with Carbon Electrodes.*—Solutions of ammoniacal salts when electrolysed in the manner above described yield a precipitate containing mellogen free from nitrogen, but no appreciable quantity of benzenecarboxylic acids could be found in the clear solution.

*Electrolysis of Ammonia with Electrodes of Graphite.*—The experiments were conducted in precisely the same manner as those first described, using, however, electrodes of purified graphite. Gas was given off from both electrodes, but only in small quantity from the positive, which became gradually disintegrated and formed a black precipitate. Mellic acid was detected in the clear supernatant liquid, which also appeared to contain pyromellic, hydromellic, and hydroxyromellic acids. The black precipitate was nothing but disintegrated graphite.

*Electrolysis of Ammoniacal Salts with Electrodes of Graphite.*—After passing a strong current for 15 days, the clear liquid was examined, but no trace of benzenecarboxylic acids or any other carbon compound could be detected. The black precipitate was a mixture of unaltered graphite with graphitic acid, and another substance analogous to graphitic oxide, sparingly soluble in alkaline and ammoniacal solutions; the yellow liquid thus obtained deposited dark red flocks when acidified.

It will be seen from the above that when ammonia solution is electrolysed, using electrodes of gas-carbon or wood-charcoal, it yields benzenecarboxylic acids, as is the case with solutions of the fixed alkalis under similar conditions, but that the black powder formed by the disintegration of the electrodes differs from mellogen in that it contains nitrogen; moreover, the authors have shown that this black substance is essentially distinct from ulmic compounds, since it yields mellic acid when treated with oxidising agents, whilst ulmic compounds do not.

C. E. G.

**Ethylic Dinitrophenylacetoacetate.** By J. HECKMANN (*Annalen*, 220, 128—146).—*Ethylic orthoparadinitrophenylacetoacetate*,



is prepared by adding a slight excess of dinitrobenzene in alcoholic solution to a mixture of sodium ethylate and ethyl acetoacetate in their molecular proportions. The liquid is kept at a temperature of 20—25° for a week; at the end of this time it will have lost its alkaline reaction, and on the addition of water ethylic dinitrophenylacetoacetate will be precipitated. If a higher temperature is employed, a portion of the ethylic dinitrophenylacetoacetate is decomposed. The crude product is purified by recrystallisation from warm alcohol. Unaltered dinitrobenzene is removed by dissolving the crystals in cold dilute potash, and rapidly reprecipitating with dilute hydrochloric acid. The pure ethylic salt crystallises in amber-coloured prisms or plates, which appear to belong to the triclinic system. The crystals are soluble in warm alcohol, ether, benzene, and chloroform. They melt at 94°, and decompose at a higher temperature with slight detonation. On boiling with water containing 10 per cent. of sulphuric acid, *orthoparadinitrophenylacetic*, carbonic, and acetic acids, and dinitrotoluene melting at 70° are formed. *Dinitrophenylacetic acid*,  $\text{C}_6\text{H}_3(\text{NO}_2)_2.\text{CH}_2.\text{COOH}$  [ $\text{CH}_2.\text{COOH} : \text{NO}_2 : \text{NO}_2 = 1 : 2 : 4$ ], crystallises in pale yellow needles melting at 160°. Ethylic dinitrophenylacetoacetate dissolves without decomposition in cold dilute alkalis, but on boiling with alcoholic potash the solution blackens and decomposition ensues, a black amorphous acid being produced, together with a white crystalline compound of the composition  $\text{C}_{24}\text{H}_{18}\text{N}_6\text{O}_{15}$ , melting at 105.5°, which is sparingly soluble in boiling alcohol. The crystalline substance dissolves in dilute potash or soda, forming a blue solution, and is reprecipitated by carbonic acid. On shaking a solution of the substance in benzene with alcoholic potash, the compound  $\text{C}_{24}\text{H}_{16}\text{K}_2\text{N}_6\text{O}_{15}$  is obtained in golden plates, which explode when heated. The crystals are soluble in water, yielding a blue solution.

The black compound mentioned above is also formed by the action of alcoholic potash on the preceding substance or on dinitrophenylacetic acid. It appears to have the composition  $\text{C}_{48}\text{H}_{32}\text{N}_6\text{O}_{19}$ , and to yield a silver salt,  $\text{C}_{48}\text{H}_{29}\text{Ag}_3\text{N}_6\text{O}_{19}$ , containing 3 mols.  $\text{H}_2\text{O}$ .

W. C. W.

**Azylines.** By E. LIPPMANN and F. FLEISSNER. Third Memoir. (*Monatsh. Chem.*, 4, 788—799).—The action of methyl iodide on diethylanilinazylene is very different from that of ethyl iodide (*Abstr.*, 1883, 868). On heating the azyline with 4 mols. methyl iodide in a sealed tube at 100°, dissolving the resulting crystalline mass in water, evaporating to a syrup, repeatedly boiling with water the resinous substance which separates out, evaporating the solutions thereby obtained to the crystallising point, and repeatedly precipitating with alcohol, white shining four-sided needles are obtained, melting at 218°, and consisting of the *di-iodomethylate of dimethyl-diethyl-paraphenylenediamine*,  $\text{C}_{14}\text{H}_{26}\text{N}_2\text{I}_2 = \text{C}_6\text{H}_4(\text{NMe}_2)(\text{NEt}_2).2\text{MeI}$ , or rather perhaps *tetramethyl-diethyl-paraphenylammonium iodide*,  $\text{NMe}_3.\text{I}.\text{C}_6\text{H}_4.\text{NEt}_2.\text{MeI}$ . This iodide dissolves very easily in water,

sparingly in alcohol, and not at all in ether. It is not attacked by strong potash-lye, but silver oxide decomposes it immediately, forming the corresponding hydroxide  $C_{14}H_{26}N_2(OH)_2$ .

When diethyl-*p*-phenylenediamine is treated with methyl alcohol and hydrochloric acid at  $200^\circ$ , the contents of the tube precipitated with potash, and the separated oil dried and fractionated, diethyldimethyl-*p*-phenylenediamine,  $NEt_2.C_6H_4.NMe_2$ , is obtained, as a faintly yellow oil, which turns brown in the air, and exhibits a deep blue colour with oxidising agents, *e.g.*, copper sulphate, potassium dichromate, iodine, bleaching powder, &c. This base, heated with methyl iodide, is converted into the compound  $C_{14}H_{26}N_2I_2$  above described.

*Oxidation*.—Azylines are but slightly attacked by weak oxidising agents, undergoing no alteration on exposure to the air at ordinary temperatures, and very little when heated above their melting points. Potassium permanganate acts on them but slowly in alkaline, very quickly in acid solution. Chromic acid, manganese dioxide, and sulphuric acid, as well as lead dioxide, act on them with violence. With potassium permanganate, the chief products formed are acetic, carbonic, and oxalic acids. With chromic acid or a mixture of potassium dichromate and sulphuric acid, the liquid froths, emits a peculiar odour like that of chlorine, and deposits a small quantity of yellow needles, easily volatile with water-vapour, very soluble in ether: probably quinone.

When diethylanilinazyline is slowly added to well-cooled red nitric acid of sp. gr. 1.5, it dissolves, and the solution diluted with water deposits shining red needles of dinitrodiethylaniline,  $C_6H_3(NO_2)_2Et_2N$ , contaminated with brown products. The same compound is, however, more easily and abundantly obtained by adding ordinary strong nitric acid to a well-cooled solution of the azyline in glacial acetic acid, then precipitating with water, and crystallising from alcohol. The compound thus obtained forms orange-red needles melting at  $180^\circ$ , easily soluble in hot alcohol, also in benzene and in ether, sparingly in light petroleum. In these and all its other characters it agrees with the dinitrodiethylaniline which von Romburgh obtained (*Rec. Trav. Chim.*, **2**, 35; *Ber.*, **16**, 1496) by the action of red nitric acid (sp. gr. 1.48) on diethylaniline dissolved in strong sulphuric acid. By boiling with potash, it is resolved into diethylamine and dinitrophenol:  $C_6H_3(NO_2)_2.NEt_2 + KHO = NHEt_2 + C_6H_3(NO_2)_2.OK$ . The authors found that this decomposition is effected only by very strong potash-lye, and that it is accompanied by the evolution of ammonia and diethylamine. According to Romburgh, the dinitrophenol produced in this reaction is the ordinary modification  $OH:NO_2:NO = 1:2:4$ ; consequently the two nitro-groups in the corresponding aniline derivatives must be similarly situated [ $NH_2:NH_2:NO_2 = 1:2:4$ ].

**AZYLINES OF TERTIARY DIPHENYLAMINES.**—These compounds are formed by passing nitrogen dioxide through an alcoholic solution of a tertiary diphenylamine, the liquid then turning red, and yielding after some time a crystalline deposit of the azyline, mixed with coloured secondary products, which greatly diminish the yield of the azyline. They are weak bases, forming neither salts nor double com-

pounds. With hydrochloric acid they give a blue-violet, with acetic acid, a green coloration, both these reactions being very delicate.

*Methyldiphenylaminazyline*,



forms yellow crystals, melting at  $150^\circ$ , very slightly soluble in cold alcohol, freely in chloroform and benzene.

*Ethyldiphenylaminazyline*,



separates from alcoholic solution in large red monoclinic crystals, exhibiting the combination  $0\text{P.P.}\infty\text{P}$  and the opposite faces. Axial ratio  $a : b : c = 0.206106 : 1 : 1.1826$ . Angle  $ac = 92^\circ 29' 30''$ . Double refraction very strong. H. W.

**An Aromatic Glycol.** By G. ROUSSEAU (*Ann. Chim. Phys.* [5], 28, 145—198).—Of the  $\alpha$ - and  $\beta$ -naphthols, the latter alone yields a hydroxyaldehyde when heated with chloroform and alcoholic potash (Reimer and Tiemann's reaction); but only one such compound is obtained, and not a mixture of two isomerides (comp. Abstr., 1882, 735, 1211, 1299). During the course of the reaction, large quantities of resinous substances are formed, from which the aldehyde may be separated by steam distillation. The aldehyde crystallises in slender refractive needles, which melt at  $77^\circ$ . Its ethereal solution gives a crystalline magma with sodium hydrogen sulphite; it combines also with aniline, yielding a yellow crystalline compound melting at  $90^\circ$ . The principal product of the reaction is, however, an *aromatic glycol*,  $\text{C}_{22}\text{H}_{12}(\text{OH})_2$ , formed probably by the partial hydrogenation of the hydroxyaldehyde, two molecules of which combine together with elimination of two molecules of water. This glycol forms small white crystals, which are with difficulty separated from the adhering resins; it is insoluble in alkalis, soluble in concentrated sulphuric acid, with production of a blood-red solution, from which red crystals of an ethereal sulphate separate out. This glycol and its immediate derivatives are characterised by the readiness with which they are transformed into the corresponding ether,  $\text{C}_{22}\text{H}_{12}\text{O}$ ; in this respect the glycol is analogous to the pinacones. The *bromhydrin* has been already described (*loc. cit.*, 1299); it takes up a molecule of bromine, yielding the compound  $\text{C}_{22}\text{H}_{12}\text{Br}(\text{OH}).\text{Br}_2$ , which crystallises in yellow leaflets resembling lead iodide, and decomposes at  $280^\circ$  without melting. The chlorhydrin,  $\text{C}_{22}\text{H}_{12}\text{Cl}(\text{OH}).\text{HCl.3OH}_2$ , crystallises in red needles. Both the brom- and chlor-hydrin, when dissolved in acetic acid, yield on evaporation of the solution a crystalline substance, consisting of a molecule of the haloid ether and a molecule of acetic acid.

The *ether*,  $\text{C}_{22}\text{H}_{12}\text{O}$ , can be obtained by the action of dehydrating or reducing agents on the glycol, or by boiling the ethereal derivatives with alcohol; it crystallises in pale yellow needles which melt at  $198^\circ$ , insoluble in cold alcohol, readily soluble in acetic acid. By the action of hydrogen, it is converted into the *monohydroxyl alcohol*,  $\text{C}_{22}\text{H}_{13}\text{OH}$ . The *monethyl* derivative of the glycol,  $\text{C}_{22}\text{H}_{12}(\text{OH}).\text{OEt}$ , prepared

by decomposing the chlor-, brom- or iod-hydrin with alcoholic potash, forms small feathery crystals, which by solution in benzene and subsequent evaporation is separable into two substances, the one melting at  $250^{\circ}$ , and probably identical with the monhydroxyl alcohol, the other crystallising in brilliant leaflets, melting at  $144^{\circ}$ , or the ethyl derivative.

The amido-derivative,  $C_{22}H_{12}(OH).NH_2$ , obtained by the action of ammonia on the bromhydrin, crystallises in slender colourless needles; it acts as a weak base, combining with hydrochloric or hydrobromic acids to form crystalline salts, of which the hydrochloride yields a platinochloride salt, crystallising in golden needles. Both the hydrochloride and hydrobromide are converted into the ether when boiled with alcohol.

The *monoatomic alcohol*,  $C_{22}H_{13}O_{11}$ , alluded to above, is one of the products of the reaction of chloroform with alcoholic potash on  $\beta$ -naphthol, but is best prepared by the action of reducing agents on the chlor- or brom-hydrin. It crystallises in silky needles, which decompose at  $260^{\circ}$ . When heated with the haloid acids, it is probably retransformed into the halogen derivatives of the glycol.

The glycol, when heated to a red heat with soda-lime, is decomposed into carbonic anhydride and a dinaphthyl, probably identical with the compound obtained by Watson Smith by passing naphthalene vapour through a red-hot tube (comp. Trans., 1879, 224—232).

V. H. V.

**Colocynthin.** By G. HENKE (*Arch. Pharm.* [3], 21, 200—205).—The bitter principle of colocynth, or *Citrullus colocynthus*, was obtained by Walz in the following manner:—The colocynth was exhausted with alcohol (sp. gr. 0.40) and the residue from the evaporation of the alcoholic solution dissolved in cold water, and precipitated with lead acetate. The lead was removed from the filtrate by sulphuric acid, and the liquid precipitated with tannic acid. This precipitate, after being dried, was dissolved in alcohol, and the tannic acid precipitated by lead acetate; the lead was then removed from the filtrate, and the solution digested for some time with animal charcoal. The filtrate from this solution evaporated to dryness and extracted with ether, left a residue of colocynthin. This was subsequently slowly deposited from a solution in alcohol in yellowish-white tufts of crystals. Its formula was found to be  $C_{56}H_{42}O_{23}$ . It was soluble in 8 parts of cold and 6 parts of hot water. By treatment with acids, colocynthin was said to yield a sugar having the formula  $C_{12}H_{10}O_{10}$ , and colocynthein,  $C_{44}H_{32}O_{13}$ , which is soluble in ether. The author attempted to extract colocynthin by a similar process, with the difference that the tannate of colocynthin was decomposed by evaporation with freshly precipitated lead carbonate, and the colocynthin extracted from the dry residue with absolute alcohol. The colocynthin obtained by this method is in the form of a light yellow powder, which could not be crystallised. It is without action on litmus, insoluble in chloroform, ether, benzene, carbon bisulphide, and light petroleum, but soluble in 20 parts of cold and 16 parts of hot water. It is also soluble in alcohol, and is reprecipitated in white flocks on adding ether. Concentrated sulphuric acid dissolves it in the cold, producing a deep red solution; the colo-



cynthin is carbonised by heating this solution. Dilute sulphuric acid has no action. The aqueous solution of colocynthin easily reduces Fehling's solution. Concentrated hydrochloric and nitric acids both dissolve colocynthin, forming coloured solutions, and on boiling the hydrochloric acid solution a dark green greasy substance is precipitated, which after being dried over sulphuric acid, is only partly dissolved by ether. The hydrochloric acid solution from which this substance was obtained reduces Fehling's solution. The author considers that these experiments, as far as they go, fail to confirm the results previously obtained by Walz. W. R. D.

**Laserpitin.** By R. KÜLZ (*Arch. Pharm.* [3], 21, 161—175).—The author has made an investigation to determine the nature of the bitter principle *laserpitin*, which is contained in the root of *Laserpitium latifolium*, or white gentian root, and to discover the connection (if any) which obtains between this substance and the bitter principles contained in other umbelliferous plants.

*Laserpitin*.—The finely sliced root was extracted by boiling with light petroleum, and on evaporating the solution *laserpitin* was deposited in crystals belonging to the monoclinic system. These were purified by recrystallisation from light petroleum, and were found to contain no water of crystallisation. *Laserpitin* melts at  $118^{\circ}$ , is insoluble in dilute acids or alkalis, but is easily soluble in chloroform, ether, benzene, and carbon bisulphide. Concentrated acids decompose it, sulphuric acid dissolving it with the production of a deep red colour. This same colour is observed when *laserpitin* is boiled with concentrated hydrochloric acid, or with alcoholic potash.

A series of combustions of the pure *laserpitin* gave numbers pointing to the formula  $C_{15}H_{22}O_4$ . No chloride or bromide of *laserpitin* could be obtained, but an acetate,  $C_{15}H_{22}O_4 \cdot \overline{AcOH}$ , crystallised in silky needles from a solution in acetic acid; even this salt was unstable. Several derivatives of *laserpitin* were obtained. An attempt to produce an acetyl derivative by the direct action of acetic chloride or acetic anhydride gave negative results.

When *laserpitin* is distilled with zinc-dust or soda-lime, no benzene or other aromatic hydrocarbon is obtained, from which the author concludes that the molecule of *laserpitin* contains no compound constituted on the type of the closed carbon-ring.

The action of concentrated hydrochloric acid on an alcoholic solution of *laserpitin* gives rise to methylcrotonic acid, and the action of concentrated sulphuric acid yields angelic acid.\* When *laserpitin* is heated with dilute nitric acid, oxalic acid is one of the products. Ebullition with alcoholic potash yields angelic acid, and fusion with potassium hydroxide, methylcrotonic acid.

*Monacetylaserpitin*,  $C_{15}H_{21}\overline{AcO}_4$ , may be obtained by the action of acetic anhydride on *laserpitin* in presence of anhydrous sodium acetate. It crystallises in colourless needles melting at  $113^{\circ}$ , and

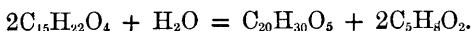
\* In another place the author mentions the production of angelic acid by the action of hydrochloric acid, and of methylcrotonic acid by the action of sulphuric acid on *laserpitin*, but from internal evidence this is probably a mis-statement.—W. R. D.

soluble in glacial acetic acid, alcohol, ether, and chloroform, but insoluble in water.

*Dinitrolaserpitin*,  $C_{15}H_{20}(NO_2)_2O_4 \cdot H_2O$ , is obtained as an amorphous mass by the action of nitric acid on *laserpitin*. It melts at  $115^\circ$ , and is insoluble in water, but soluble in alcohol, ether, chloroform, and glacial acetic acid.

*Bromolaserpitin*,  $C_{30}H_{39}Br_5O_8$ , obtained by the action of bromine on a solution of laserpitin in chloroform, crystallises in rosettes, which are soluble in ether, alcohol, chloroform, and glacial acetic acid; they melt at  $90^\circ$ .

*Lazerin*,  $C_{20}H_{30}O_5$ , is a resinous substance (called by the author *lazerol*) which is produced when concentrated acids or alkalis act on laserpitin. It is insoluble in acids, but is dissolved by ether, alcohol, chloroform, and glacial acetic acid. Its production, together with angelic acid or methylcrotonic acid, by the action of sulphuric or hydrochloric acids on laserpitin, is symbolised by the equation



Attempts to produce derivatives of this body were unsuccessful. From these results, the author infers that laserpitin is chemically different from peucedanin, ostruthin, and athamantin, bitter principles which have been found in other umbelliferous plants. W. R. D.

**Quinaldine Bases.** By O. DOEBNER and W. v. MILLER (*Ber.*, 16, 2464—2472).—Several methods for the preparation of quinaldine have been already described (*Abstr.*, 1882, 868; 1883, 602; and *Ber.*, 16, 165, and 1835), but it is most simply effected by heating on the water-bath a mixture of  $1\frac{1}{2}$  parts paraldehyde, 1 part aniline, and 2 parts hydrochloric acid; in all probability the aldehyde is first converted into aldol by the hydrochloric acid, but whether this reacts directly on the aniline, or is first converted into crotonaldehyde, remains an open question. The hydrochloric acid may be replaced by other concentrated acids, but the yield is not so good.

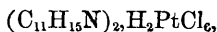
*Tetrahydroquinaldine*,  $C_{10}H_{13}N$ , is readily obtained by the action of tin and hydrochloric acid on quinaldine; it forms a colourless liquid of agreeable odour, boils at  $246$ — $248^\circ$ , at 709 mm. pressure, is sparingly soluble in water, readily soluble in alcohol, ether, and benzene. Its salts crystallise well, are generally readily soluble in water, and are characterised by the blood-red coloration produced in their aqueous solution by oxidising agents. The *platinochloride* forms clear yellow needles. Nitrous acid gives a yellow nitroso-compound; from this, hydroquinaldine must be a secondary base, standing to quinaldine in the same relation as piperidine does to pyridine, and

having the constitution  $C_6H_4 \begin{array}{c} \text{NH} \cdot \text{CH} \cdot \text{CH}_3 \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$ . A base of this formula

has been obtained by Jackson (*Abstr.*, 1881, 742) from methylphenyl ethyl ketone, which from its properties appears to be identical with tetrahydroquinaldine.

*Methyl hydroquinaldine*,  $C_{10}H_{12}NMc$ , obtained by the action of

methyl iodide on hydroquinaldine, is a colourless liquid boiling at 245—248° at 708 mm. pressure. The platinochloride,



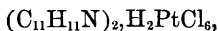
is sparingly soluble in water. Other alkyl derivatives have been obtained; they are all characterised by yielding green colouring matters when heated with benzotrichloride and zinc chloride.

*Quinaldine methiodide*,  $C_{10}H_9N \cdot MeI$ , is obtained by the direct union of methyl iodide and quinaldine; it crystallises in long citron-yellow needles, melts at 195°, is readily soluble in water and hot alcohol, insoluble in ether. When heated with concentrated potash, it yields a very small quantity of a carmine colouring matter.

*Methylquinaldines*.—On treating the isomeric toluidine in a manner similar to that already described in the case of aniline, three methylquinaldines are obtained.

*Orthomethylquinaldine*,  $C_{10}H_8MeN$  [1 : 2], is a colourless liquid, which soon turns brown on exposure to air, boils at 252°, is sparingly soluble in water, readily soluble in alcohol and ether; its odour closely resembles that of quinaldine. The *dichromate*,  $(C_{11}H_{11}N)_2 \cdot Cr_2O_7H_2$ , crystallises in orange-yellow needles, readily soluble in water. The *platinochloride*,  $(C_{11}H_{11}N)_2 \cdot H_2PtCl_6$ , forms bright yellow needles, sparingly soluble in water. *Hydro-orthomethylquinaldine*,  $C_{10}H_{12}MeN$ , is a colourless liquid of agreeable odour; it boils at 260—262°, and is characterised by the sparing solubility of its hydrochloride in hydrochloric acid. The platinochloride forms round nodules of concentrically grouped brownish-red needles. The hydro-base gives a blood-red coloration with ferric chloride, and on treatment with methyl iodide, yields a liquid methyl derivative,  $C_{11}H_{14}NMe$ .

*Paramethylquinaldine*,  $C_{10}H_8MeN$  [1 : 4], forms large colourless rhombic prisms, melts at 60°, and boils at 266—267°. It has an odour like that of aniseed, is sparingly soluble in hot water, readily in alcohol, ether, and benzene. The *dichromate*,  $(C_{11}H_{11}N)_2 \cdot Cr_2O_7H_2$ , forms long yellow needles, sparingly soluble in cold water. The *platinochloride*,



crystallises in nearly colourless slender needles, and is sparingly soluble in hot water. *Hydroparamethylquinaldine*,  $C_{10}H_{12}MeN$ , forms a colourless, mobile liquid, boils at 267°, is sparingly soluble in water, readily in alcohol and ether. Solutions of its salts give a red coloration with ferric chloride.

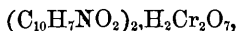
*Metamethylquinaldine*,  $C_{10}H_8MeN$  [1 : 3], crystallises in colourless needles, melts at 61°, and boils at 264—265°; is sparingly soluble in water, readily soluble in alcohol, ether, and benzene. It has a faint quinaldine-like odour. The *dichromate*,  $(C_{11}H_{11}N)_2 \cdot Cr_2O_7H_2$ , crystallises in long orange-red needles, nearly insoluble in water. The *platinochloride*,  $(C_{11}H_{11}N)_2 \cdot H_2PtCl_6$ , forms tufts of small yellow needles, sparingly soluble in water.

All primary amines of the aromatic series appear to react with aldehyde to form quinaldine-like bases, several of which are being investigated by the authors.

A. J. G.

**Quinaldic Acid ( $\alpha$ -Quinolinecarboxylic Acid).** By O. DOEBNER and W. v. MILLER (*Ber.*, 16, 2472—2476).—In their earlier experiments on the oxidation of quinaldine (Abstr., 1883, 602), the authors were unable to confine the oxidation to the methyl-group; they have now accomplished this by dissolving 10 grams of the base in sulphuric acid (1 : 5), adding a solution of 28 grams of chromic acid and 40 grams of sulphuric acid in 100 c.c. of water, and heating on the water-bath until the chromic acid is completely reduced. *Quinaldic acid*,  $C_6H_4$   $\begin{array}{l} \text{N}=\text{C}.\text{COOH} \\ | \\ \text{CH}=\text{CH} \end{array}$ , so obtained, crystallises with 2 mols.

$H_2O$  in colourless asbestos-like needles, sparingly soluble in cold, readily in hot water. The anhydrous acid melts at  $156^\circ$ . Quinaldic acid yields salts with both acids and bases, of which those with acids crystallise the best. The *sulphate* is readily soluble in water; the *nitrate* crystallises in prisms and is sparingly soluble in water containing nitric acid; the *hydrochloride*,  $C_{10}H_7NO_2.HCl + H_2O$ , forms large tables sparingly soluble in water. The *dichromate*,



forms red crystals sparingly soluble in cold water. The *picrate* crystallises in tufts of long yellow needles readily soluble in hot water and alcohol. The *platinochloride*,  $(C_{10}H_7NO_2)_2.H_2PtCl_6 + 2H_2O$ , forms tabular crystals sparingly soluble in cold, readily soluble in hot water.

The *quinaldates* of the alkalis are readily soluble in water. *Calcium quinaldate*,  $Ca(C_{10}H_6NO_2)_2$ , is obtained as a white precipitate sparingly soluble in water. The *copper salt*,  $Cu(C_{10}H_6NO_2)_2 + 2H_2O$ , forms a microcrystalline bluish-green precipitate. The *silver salt* is obtained as an amorphous precipitate, not decomposed by light; it dissolves in hot concentrated solution of silver nitrate; on cooling a double compound of the formula  $C_{10}H_6NO_2Ag + C_{10}H_7NO_2.NO_3H + H_2O$  separates in silky needles.

On heating quinaldic acid to a little above its melting point, it is quantitatively decomposed into carbonic anhydride and quinolines.

This acid completes the series of quinolinecarboxylic acids in which the carboxyl is considered to be attached to the pyridine nucleus, and from its formation from quinaldine must be the  $\alpha$ -acid.  $\beta$ -Quinolinecarboxylic acid was obtained by Riedel from  $\beta$ -ethylquinoline (*Ber.*, 16, 1613), whilst the quinolinecarboxylic acid obtained by Graebe and Caro (Abstr., 1880, 398) must have the carboxyl-group in the  $\gamma$ -position.

A. J. G.

**Caffeine and its Salts.** By H. BIEDERMANN (*Arch. Pharm.* [3], 21, 175—186).—The author has examined caffeine and its principal salts, as the existence of many of these has recently been denied by several authors. Caffeine,  $C_8H_{10}N_4O_2.H_2O$ , melts at  $230.5^\circ$ ; the aurochloride of caffeine has the formula  $C_8H_{10}N_4O_2.HCl.AuCl_3 + 2H_2O$ , and the platinochloride the formula  $(C_8H_{10}N_4O_2)_2.H_2PtCl_6$ . Caffeine hydrochloride,  $C_8H_{10}N_4O_2.HCl + 2H_2O$ ; hydrobromide,



nitrate,  $C_8H_{10}N_4O_2 \cdot HNO_3 + H_2O$ ; sulphate,  $C_8H_{10}N_4O_2 \cdot H_2SO_4$ ; formate,  $C_8H_{10}N_4O_2 \cdot H_2CO_2$ ; acetate,  $C_8H_{10}N_4O_2 \cdot (AcHO)_2$ ; benzoate,  $C_8H_{10}N_4O_2 \cdot C_6H_5O_2$ ; and valerate,  $C_8H_{10}N_4O_2 \cdot C_5H_9O_2$ , were all obtained in the crystalline state by dissolving caffeine in the appropriate acid, and evaporating the solution over potash. All these salts are unstable, and cannot be crystallised from alcohol or water; at  $100^\circ$  they are either wholly or partially decomposed. Anhydrous chlorides having the formulæ  $C_8H_{10}N_4O_2 \cdot 4HCl$  and  $C_8H_{10}N_4O_2 \cdot HCl$ , were obtained by the action of dry hydrochloric acid gas on caffeine. A normal sulphate was also obtained which crystallised with 1 mol.  $H_2O$ . When caffeine is dissolved in a strong solution of hydriodic acid and the solution evaporated over potash, the normal hydriodide is not alone obtained, but a periodide,  $(C_8H_{10}N_4O_2 \cdot HI \cdot I_2)_2 + 3H_2O$ , and also a mixture of the normal hydriodide,  $C_8H_{10}N_4O_2 \cdot HI$ , and the hydriodide,  $C_8H_{10}N_4O_2 \cdot 2HI$ . W. R. D.

**Papaverine.** By G. GOLDSCHMIEDT (*Monatsh. Chem.*, **4**, 704—707).—The oxidation of papaverine with potassium permanganate yields nothing but uncrystallisable products. On boiling this base with a somewhat dilute solution of potassium permanganate, ammonia is given off, and an uncrystallisable acid is formed which decomposes carbonates and forms amorphous salts.

Papaverine fused with potassium hydroxide yields protocathechuic acid and an alkaline distillate containing papaverine, methylamine, and dimethylhomocatechol, boiling at  $218^\circ$  and convertible by oxidation into protocatechudimethyletheric acid. The same two volatile products, dimethylhomocatechol and methylamine, are formed in the dry distillation of papaverine, and apparently also in the distillation of that base with lime or zinc-dust.

Baryta-water acts very slowly on papaverine, with evolution of ammoniacal vapours, and formation of a very small quantity of a greasy substance smelling like guaiacol. Sodium-amalgam slowly converts papaverine in alcoholic solution into a thick oil which deposits crystals after long standing. With acetic anhydride and sodium acetate, papaverine does not yield an acetyl-derivative, whence it may be inferred that this base does not contain an acetyl-group.

Papaverine, heated with hydrochloric acid in a sealed tube at  $130^\circ$ , yields a gas which burns with a green flame (probably methyl chloride) and a solution, the evaporated residue of which forms a thick brown oil which, in dilute aqueous or alcoholic solution, gives with ferric chloride a deep emerald-green coloration, changed by sodium carbonate to red—a reaction probably due to homocatechol. With potash-lye, the oil forms a dark brown liquid. Sodium carbonate added to the aqueous solution of the oil, throws down a white flocculent precipitate which soon resinises after filtration, and turns green in contact with the air. These reactions point to the presence of apomorphine. H. W.

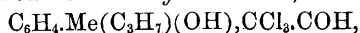
**Compound of Quinine with Chloral.** By G. MAZZARA (*Gazzetta*, **13**, 269—272).—This compound, *chloral-quinine*, is formed on adding to a solution of quinine in chloroform dried at  $120^\circ$  an

equivalent quantity of chloral (5.5 g. anhydrous chloral to 10 g. quinine). On evaporating the liquid in a dry atmosphere, a yellowish transparent gelatinous mass is left, which dissolves in cold ether; and on exposing the solution to a gentle heat, a white mammillary crystalline substance separates which soon pervades the whole liquid, converting it into a pulp. The same result is more quickly obtained on adding the calculated quantity of chloral to a solution of quinine in chloroform diluted with anhydrous ether, and heating the liquid. The precipitate, after washing with ether and drying over sulphuric acid, forms an apparently amorphous, perfectly white and very light mass, having a slightly bitter taste, melting and blackening at  $149^{\circ}$ , not perceptibly altering in dry air. This body has the composition  $C_{20}H_{24}N_2O_2, CCl_3, COH$ . It is insoluble in benzene, sparingly soluble in cold, more soluble in hot alcohol, from which it separates on evaporation as a gelatinous mass. The solution, on addition of water, deposits a white precipitate consisting of a mixture of quinine and chloral-quinine.

Chloral-quinine dissolves in water slightly acidulated with sulphuric, acetic acid, &c., forming solutions which exhibit a fluorescence similar to that of quinine salts, and react like the latter with chlorine and potassium ferricyanide. The acetic acid solution yields with sodium bicarbonate a precipitate nearly free from chlorine. These reactions show that chloral-quinine is decomposed partially by water, completely by acids.

Phenols, as is well known, do not form addition-products with chloral, but in presence of dehydrating agents they yield condensation-products with elimination of water—phenol and thymol for example, forming respectively dihydroxyphenyl- and dihydroxythymyl-trichlorethane. The author has also succeeded in obtaining addition-products by the action of chloral on paracresol and thymol, without the aid of sulphuric acid.

*Paracresol-chloral*,  $C_8H_7Me(OH), CCl_3, COH$ , crystallises in small needles melting at  $52-56^{\circ}$ . *Thymol-chloral*,



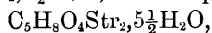
melts at  $130-134^{\circ}$ .

H. W.

### Solubility of Strychnine and Preparation of some of its Salts.

By P. CRESPI (*Gazzetta*, 13, 175).—The author has determined the solubility of strychnine at ordinary temperatures and at  $56^{\circ}$ ,  $78^{\circ}$ , and  $98.5^{\circ}$  in various solvents. He finds that 1 pt. of water at  $14.5^{\circ}$  dissolves 0.025 pt. of strychnine; that 1 pt. absolute alcohol dissolves from 0.302 to 0.325 at  $8.25^{\circ}$  and  $10.75^{\circ}$ ; 0.975 at  $56^{\circ}$  and 1.846 at  $78^{\circ}$ ; that amyl alcohol, one of the best solvents, dissolves 0.525 at  $11.75^{\circ}$ , and 4.262 at  $98.5^{\circ}$ ; that its solubility in dilute alcohol increases with the proportion of water up to  $85^{\circ}$  of Gay-Lussac's areometer, and diminishes at greater dilution.

The salts described are the normal succinate,  $C_4H_4O_4Str_2, 6\frac{1}{2}H_2O$ ; normal malate,  $C_4H_6O_5Str_2, 3\frac{1}{2}H_2O$ ; normal pyrotartrate,



and the phthalate which has not been analysed.

H. W.

**Behaviour of Strychnine in the Animal Organism; and a Product of the Action of Potassium Permanganate on Strychnine.** By PLUGGE (*Chem. News*, 48, 207).—The contention as to whether alkaloids do or do not undergo decomposition in the animal organism has never been definitely settled. Kerner (*Pflüger's Archiv.*, 2, 20; 3, 30) proved that quinine in part reappears unchanged in the urine, whilst another portion becomes oxidised into dihydroxyquinine, a substance which is also obtained by the action of potassium permanganate on quinine. The author has made similar experiments with strychnine. Strychnine was given to animals; and the blood, tissues, and urine were examined. The results obtained indicate that the strychnine is decomposed in the organism, but the investigation is incomplete.

By the action of potassium permanganate on strychnine, a yellowish-brown or light grey amorphous substance is obtained. It is sparingly soluble in cold water, ether, and chloroform, more freely in hot water, from which it is partially deposited on cooling; readily soluble in alcohol, and very readily in dilute aqueous alkaline solutions, from which it is incompletely reprecipitated by adding hydrochloric acid. The substance is neither bitter nor poisonous, and is not precipitated by the usual alkaloid reagents. Treated with chromic mixture, it gives a red-violet coloration without the preliminary blue-violet, as is the case with strychnine. The author regards this strychnine-derivative as strychnic acid, to which he assigns the formula  $C_{11}H_{11}NO_3 \cdot H_2O$  for the present.

D. A. L.

**Alkaloids of *Buxus sempervirens*.** By G. A. BARBAGLIA (*Gazzetta*, 13, 249—257).—The author has extracted from the leaves and twigs of the box tree, a substance which he regards as a new alkaloid, and designates by the name *Buxidine*. He denies the existence of the base called *Buxine* described by Alessandri (*C. J.*, 1882, Abstr., 745) as existing in the same plant. His results however are not very definite.

H. W.

**Acid Products of the Bacterial Fermentation of Albuminoids.** By A. GAUTIER and A. ÉTARD (*Compt. rend.*, 97, 325—328).—When the products of putrefaction are distilled to dryness in a vacuum, and the residue extracted with ether, the principal constituent of the solution (this vol., p. 89) is palmitic acid. Neither stearic nor oleic acid is present, and all traces of the original fatty bodies, and all the corresponding glycerol, have completely disappeared. Stearic acid is, however, represented by a small quantity of amidostearic acid (*loc. cit.*). The acid products of the putrefaction of albuminoids are—

- |                                     |          |        |                          |
|-------------------------------------|----------|--------|--------------------------|
| (I.) <i>Fatty series</i> . . . . .  | Formic   | acid.. | Very small quantity.     |
|                                     | Acetic   | „ ..   | Doubtful.                |
|                                     | Butyric  | „ ..   | Large proportion.        |
|                                     | Valeric  | „ ..   | Smaller proportion.      |
|                                     | Palmitic | „ ..   | Abundant.                |
| (II.) <i>Acrylic series</i> . . . . | Acrylic  | „ ..   | Small quantity.          |
|                                     | Crotonic | „ ..   | Considerable proportion. |

(III.) <i>Lactic series</i> . . . . .	Glycollic acid	Moderate quantity.
	Lactic(ord.) „	Small quantity.
	Valerolactic „	Doubtful.
(IV.) <i>Oxalic series</i> . . . .	Oxalic „	Trace.
	Succinic „	Large quantity.
	Carbonic „	Large quantity.
(V.) <i>Nitrogenous acids</i> ..	$C_9H_{15}NO_4$ . . . . .	Moderate quantity.
	Amidostearic acid	Small quantity.
	Leucines and luceïnes.	Abundant.

C. H. B.

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## Physiological Chemistry.

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**Chemistry of Perspiration.** By ST. CAPRANICA (*Gazzetta*, 13, 171).—To establish the analogy between the kidneys and sudorific glands, the author has endeavoured to ascertain whether creatinine, which is known to be a normal constituent of urine, exists also in the perspiration. On evaporating 450 c.c. perspiration in a vacuum to one-fifth of its bulk, precipitating with absolute alcohol, filtering, evaporating, and testing the residue by Will's process, he succeeded in demonstrating the presence of creatinine. On the other hand, he does not think that any such relation exists between uric acid and sudoric acid,  $C_{10}H_{16}N_2O_{13}$ , but he regards the latter as a product of the oxidation of glutamic acid ( $2C_5H_9NO_4 + O_5 = H_2O + C_{10}H_{16}N_2O_{13}$ ), and as probably identical with the cryptophanic acid which Thudichum found in urine.  
H. W.

**Substitute Values of the Chief Organic Alimentary Principles in the Animal Body.** By M. RUBNER (*Zeitschr. Biol.*, 19, 313—496).—Previous investigations on this subject by Pettenkofer and Voit (*Zeitschr. Biol.*, 7, 433; and 9, 1 and 435) formed the starting point of the author's researches. His experiments were carried out similarly on the dog. He employs the term *isodynamic* in connection with those principles which are capable of replacing one another, as being more precise than the expression *equivalent*, which has a wider application.

Alimentary fat is isodynamic in equal weight with the body fat. On feeding with fat, loss of weight in fat is arrested by exactly the same amount as food which would otherwise have been consumed as body fat. Alimentary fat, when of the same composition as that of the animal body, is transformed into the latter with facility. Muscle-flesh as food (circulating albumin) is isodynamic in equal weight with the albuminoid material of the body, which upon insufficient supply of albumin in food becomes consumed (disintegrated organic albumin).

During starvation, when the fat of the body disappears, the organic

albumin becomes disintegrated in amount, corresponding with the calorificient value of the previously consumed fat.

The actual value in respect of capacity for heat-production of unorganised or dead albumin and living or organised albumin, is the same. Hence it is extremely probable that the formation of the latter from the former takes place without any accumulation of potential energy.

Fats and carbohydrates, as regards force-producing value, differ for equal weights, 100 parts of fat corresponding on the average with 240 parts of carbohydrate. The isodynamic values for albumin and carbohydrates may be determined from those of fat and albumin on the one hand, and fat and carbohydrates on the other, from which it appears that 100 parts of dried albumin are isodynamic with 110 parts of cane-sugar or 122 parts of grape-sugar. The limits within which a replacement or substitution of one principle for another may take place are very wide.

Hitherto it has been accepted that the alimentary principles replace one another according to definite chemical proportions. The present investigation places beyond doubt that the isodynamic value of these is the expression of equal intrinsic energy.

In the following table, in which the calorificient values of alimentary substances is given after the statements of Danilewsky and Rechenberg, it will be seen that the individual isodynamic values of these differ to an unimportant extent from the results of direct calorimetric determinations.

100 parts of fat corresponding with:—

	By direct experiment on the animal.	By calorimetric de- termination.
Albumin.....	211	201
Starch.....	232	221
Cane-sugar.....	234	231
Anhydrous grape-sugar ....	256	243
Ordinary grape-sugar.....	282	271

The results of experiments in the animal are somewhat higher than those calculated, the difference being due to several causes, such as, in the case of albumin and starch, putrefactive and fermentative changes in the intestine, whereby a loss of potential energy is occasioned, whilst in the case of carbohydrates, the work done by the muscles of respiration being increased, the excretion of  $\text{CO}_2$  is also increased, and proportionately to a greater degree than in the case of fat itself, thereby accounting for the somewhat lower value of each of the carbohydrates in comparison with fat.

Assuming that the substitution of alimentary principles was effected according to the amount of oxygen which these required for their oxidation, it is of interest to consider how the isodynamic values as determined in the animal, compare with the values which would thus be obtained.

This is shown in the following table:—

100 parts of fat correspond with—

	According to oxygen con- sumed.	According to experiment in the animal.	According to calorimetric determination.
Albumin.....	193	211	201
Starch.....	240	232	221
Cane-sugar.....	249	234	231
Grape-sugar.....	263	256	243

Excepting albumin, the alimentary principles exhibit lower values than that obtained by calculating the oxygen required for combustion. As the conditions of direct experiment tend rather to yield higher values than otherwise, it is apparent that the capacity of those principles for equivalent amounts of oxygen is not a measure of their capacity for substituting or replacing each other.

Whilst the experiments show this replacement or substitution of one alimentary principle for another, according to the amount of heat-production which is afforded by their combustion in the body, it is not implied that they replace each other because they yield the same amount of heat. The heat-production is only a measure of the total potential energy of the principle, and the isodynamic values indicate only alimentary principles of equal potential energy. A knowledge of these isodynamic values allows of measurement of any given kind of tissue change, and by adding together the calorific values of the disintegrated tissues, a numerical expression for the whole is obtained. This expression may take the form of so much albumin, fat, or a carbohydrate, but more appropriately of heat-units, as best corresponding to the essence of the process itself.

The greatest part of all these processes, included under the definition of tissue-change, is in effect an exchange of energy.

Within a small fraction of the total disintegration, it is quite indifferent as to what alimentary principles we introduce into the body. As regards albumin, only a trifling amount is incapable of being replaced by isodynamic quantities of other principles. To this amount the addition of albumin cannot be dispensed with, for there is a constant loss going on of epidermis and hair from the surface, of blood corpuscles, of epithelium in the intestine, and of nitrogenous secretions from the glands. For the renovation of such, processes of growth and maintenance are necessary, while it is easy to show that these processes participate only to an insignificant extent in the total interchange of energy.

What takes place in the organism as a whole may be regarded as taking place in each of its component cells, and that in the individual cell element, one alimentary principle substitutes another according to the proportion of its potential energy.

Albumin is to be regarded as the most readily decomposable principle, a fact which has already been established by the experiments of

Pettenkofer and Voit, although in apparent contradiction to observations as to its comportment outside the body, which tended to show the more difficult disintegration of albumin in comparison with fats and carbohydrates. In the body, the latter exhibit a different relation, the fats being more difficultly oxidisable than the carbohydrates; of course it may be assumed that there is no essential distinction of this kind, which may be accounted for by the readier solubility of the carbohydrates in the juices, whereby in simultaneous feeding with both principles, these are the first to be subjected to disintegration.

D. P.

**On the Digestion of Cows' Milk, and on the Substances which increase its Digestibility.** By J. UFFELMANN (*Bied. Centr.*, 1883, 315—319).—The points considered were—(1) behaviour of milk with hydrochloric acid, lactic acid, and artificial gastric juice; (2) behaviour in the alimentary canal; (3) digestibility of boiled milk and buttermilk; (4) methods of rendering milk more easily digestible. The precipitate formed by a 2 per cent. solution of hydrochloric acid in milk assumes either a fine or heavy flocculent condition, or also cheesy, according to the conditions of mixing, which are, however, not readily ascertained, as variations in the form of the precipitate occur, the reason for which is not apparent. The action of lactic acid is similar to that of hydrochloric acid. The lumpy condition of the curd which is produced by 4 parts acid (2 per cent.) to 5 milk is not readily digested by pepsin, and if an insufficiency of acid produces no curd in the cold, then the addition of pepsin to the warm liquid causes the production of firm and compact curd. Small quantities of lactic acid have no influence on the digestion, but large quantities retard the action of pepsin. The digestive coefficients of milk in the bodies of adults and infants are as follows:—

	Adults.	Infants.
Dry matter....	90—91·7	90—94
Albumin.....	98·4—99·2	98·2—99·4
Fat .....	93·4—95·6	92·2—94·9
Sugar .....	100	100
Salts .....	44·2—56·6	45·4—57

Of the calcium salts only 25—30 per cent. are digested, whereas in human milk the percentage is 75—80. By boiling milk all the gases are removed, as well as some odorous substance; when the boiling is conducted in an open vessel a skin is formed; this skin is not all casein, but has the following constitution:—

	In 1·506 grams.	In 1·086 grams.
Fat.....	0·617	0·283
Albumin ..	0·820	0·751
Sugar.....	0·062	0·046
Salts .....	0·007	0·006

The author does not find boiled to be more digestible than unboiled milk. From buttermilk a curd is formed by hydrochloric acid, which

is readily dissolved by gastric juice. Of the additions generally made to milk, such as arrowroot, yolk of eggs, &c., to render it more digestible, barley-water is the best, and experimentally it has been shown that the coefficient for albumin is raised to 99.75 by its use.

E. W. P.

**Relative Absorption of Neutral Salts in the Human Stomach.** By W. JAWORSKI (*Zeitschr. Biol.*, 19, 397—445).—These experiments were carried out under normal physiological conditions in a healthy man who drank the solutions (500 c.c.) of chemically pure salts and remained at rest until the residual fluid was recovered from the stomach by means of an aspirating pump specially devised for the purpose. This was then submitted to analysis, and the changes in the percentage of the salts determined.

These investigations showed that in the human stomach the absorption of individual salts is different, and dependent upon their chemical composition.

The acid carbonates (magnesium and sodium) underwent the greatest, the chlorides (magnesium, potassium, sodium, and ferric) the least absorption, and the sulphates (sodium and magnesium) between these extremes.

The difference in the absorption of two salts is the greater the longer the solution is present in the stomach.

The presence of acids in the stomach hastens absorption, and the difference in the absorption of individual salts becomes more pronounced. Carbonic acid especially accelerates absorption, which, on the other hand, is hindered by alkalinity of the contents of the stomach.

The presence of common salt neither accelerates absorption nor increases the gastric secretion; the action is negative in both directions.

The secretion of chlorine is greater in proportion to the alkalinity of the saline solution and the length of time the latter remains in the stomach. Acid sodium carbonate excites the secretion of the gastric mucous membrane less than the neutral carbonate.

When distilled water is introduced into the stomach, secretion of acid contents (hydrochloric acid) ensues, and that in proportion to the lowness of its temperature.

Should a salt undergo dissociation of its acid and base in the stomach, these are not absorbed in the ratio of their combining proportions. Saline solutions may be found on aspiration still present in the stomach an hour after their introduction, whereas the same quantity of distilled water disappears almost entirely within half an hour afterwards. From these results certain practical suggestions of clinical importance may be derived.

In the first place the administration of salts in the form of acid carbonates, as with an excess of carbonic acid, is advantageous, for absorption takes place more quickly, and with a more rapid emptying of the stomach there is less irritation of its mucous membrane. The author observed the action of  $\text{CO}_2$  and of the acid carbonates, as also of  $\text{CaH}_2\text{CO}_3$  in a series of experiments with acidulous mineral waters.

Alkaline fluids, on the other hand, delay absorption and the evacuation of the stomach, and the gastric walls are stimulated to secretion more strongly than by other solutions. Acids favour absorption and rapid evacuation of the gastric contents.

The presence of common salt in the stomach does not appear to offer the advantages in regard to digestion which have heretofore been ascribed to it, neither stimulating to greater excretion of the gastric acid (this remark may perhaps not apply to pepsin) nor to evacuation of its contents. In the moderation of the activity of the gastric walls by alkaline agents may probably be found an explanation of the therapeutic results of certain remedies, such as magnesium carbonate, sodium carbonate, and certain metallic oxides, in relieving the pain of cardialgia.

The introduction of salts in the form of chlorides in neutral solution is, as regards gastric absorption, not advantageous, and still less so in the case of neutral carbonates, which are absorbed only in proportion as their transformation into chlorides takes place.

The difficult absorptivity of ferrous chloride is especially to be noted from a medical point of view, and considering the facility of absorption of acid carbonates, it may be assumed that an acid ferrous carbonate would prove the most absorbable of all iron preparations.

D. P.

#### **Basic Phosphate of Lime as an Addition to Cattle Fodder.**

By COHN (*Bied. Centr.*, 1883, 428).—The author has reviewed several experiments in this direction, and thinks that the addition of the substance, not only to medicines for cattle but to their ordinary fodder, would be very beneficial. He recommends for lambs and young pigs 8.12 grams, for calves and foals 12.20 grams, for oxen and cows 20.25 grams per head per day.

J. F.

**Influence of Distillers' Waste on Milk Secretion.** By M. SCHMOEGER and O. NEUBERT (*Bied. Centr.*, 1883, 312—314).—The full details of the experiments are given, and the results were that distillers' waste (maize) greatly increased the yield of milk, but hardly affected the percentage of fat present. It is consequently a more remunerative food than brewers' grains.

E. W. P.

**Colouring-matters of the so-called Bile of Invertebrates, and of the Bile of Vertebrates, and some unusual Urine Pigments, &c.** By C. A. MACMUNN (*Proc. Roy. Soc.*, 35, 370—403).—The author's observations lead him to conclude that the liver of Invertebrates discharges other functions besides those of a pancreas, which biologists generally regard it.

The colouring-matter of the bile in vertebrates does not occur in invertebrata, with the single exception of hæmochromogen, which is found in *Astacus fluviatilis* and the pulmoniferous mollusca.

Hoppe-Seyler had failed to detect bile pigments and bile acids in invertebrates. In the present instance, the animals submitted to investigation were taken from the sub-kingdoms, Mollusca, Arthropoda, and Echinodermata. The most striking result of this examination has been the discovery of a chlorophyll pigment in Mollusca and

some Arthropoda, and amongst echinoderms in the radial appendages or cœca of starfishes. This pigment, occurring in the appendages of the enteron, has been termed *enterochlorophyll* by the author, in preference to *zoochlorophyll*, as more precisely defining the location of the chlorophyll which has been found in the mantle or integument of certain invertebrates.

Enterochlorophyll was not discovered in *Lumbricus*, *Hirudo*, or *Aphrodite*, amongst *Vermes*.

In this inquiry reliance as to the identity of the pigment under consideration with that occurring in plants has been placed on spectroscopic and chemical tests, the author accepting the dictum of Vogel and Kundt, that if colouring-matters dissolved in the same medium yield identical spectra, and present identical changes of spectra when acted on by the same reagent, the colouring-matters are themselves identical.

As a standard of reference for the spectral bands obtained from the pigment of invertebrates, the measurements of the bands of the first half of the spectrum yielded by the chlorophyll of the leaves of *Primula* are given.

An alcohol-ether extract gave four bands:—

1st band	$\lambda$ 674	—643
2nd	„ $\lambda$ 622.5	—602
3rd	„ $\lambda$ 590.5	—567
4th	„ $\lambda$ 548	—530

The residue left by this extract on evaporation and dissolved in rectified spirit, gave a series of five bands:—

1st band	$\lambda$ 684	—634
2nd	„ $\lambda$ 618	—598
3rd	„ $\lambda$ 586	—570
4th	„ $\lambda$ 546.5	—534
5th	„ $\lambda$ 484	—465

and this solution treated with nitric acid yielded—

1st band	$\lambda$ 661	—646
2nd	„ $\lambda$ 608	—592
3rd	„ $\lambda$ 576	—561
4th	„ $\lambda$ 539	—521
5th	„ $\lambda$ 502	—484?

With this latter series of five bands the spectrum yielded by the bile-colouring matters of the lamellibranchiate mollusca, examined under similar conditions of solution in alcohol and treatment with nitric acid, was identical. The molluscs included in this part of the investigation were the common oyster, mussel, and cockle, also *Anodon* and *Unio*. Hence it is concluded that the chlorophyll of leafgreen and their bile pigments are identical. It was proved that the colouring matter of the molluscan liver was not due to the presence of parasitic algæ. Negative results were obtained on treating the extracts with ammonium sulphide, showing hæmoglobin to be absent.

Of Cephalopoda, the common squid, *Octopus vulgaris*, only was examined. The results were essentially the same, the five-banded spectrum being yielded by the colouring-matter of the liver on treatment with nitric acid. Some slight differences observable appear to the author to be due to the presence of the pigment in a more highly oxidised state than in other cases, perhaps as an acid enterochlorophyll. Among gasteropod mollusca, species of whelk were examined, including *Buccinum undatum*, *Fusus antiquus*, *Purpura Lapillus*, and *Litorina litorea*, with corresponding results. In the case of *Purpura Lapillus*, which possesses the well-known purple-producing glands, it was noted that there was no peculiarity of the colouring-matter obtained from the liver, which yielded enterochlorophyll alone.

The investigation of the pulmoniferous mollusca embraced several species of snail, *Helix aspersa*, *H. pomatia*, and others; also of slugs, *Limax flavus*, and *Planorbis*.

In these, with the exception of *Planorbis*, which contains abundance of hæmoglobin, hæmochromogen (reduced hæmatin) was invariably present, in addition to chlorophyll, the author thereby confirming the previous observations of Sorby, who did not, however, notice the latter pigment. The spectrum of hæmochromogen was yielded by the bile, both with and without treatment with ammonium sulphide. Its presence may be dependent upon aerial respiration, and this resemblance of molluscan to mammalian bile in respect of the presence of hæmochromogen is of interest. The respective bands of the two colouring-matters extended generally, the reduced hæmatin first band,  $\lambda$  570—566, second  $\lambda$  539—526, and the enterochlorophyll  $\lambda$  678—661. The bands of reduced hæmatin are not always in quite the same position.

Of Arthropoda, some species of crab, and the common lobster, *Homarus vulgaris*, were examined. Enterochlorophyll was less satisfactorily found, although present in most instances, than in the instance of the mollusca. In *Carcinus mænas* its presence was, however, exceptional, while that of a lutein pigment appeared to be constant.

The common crayfish, *Astacus fluviatilis*, alone yielded evidence of the presence of hæmatin in the bile, and this in considerable amount. No other crustacean showed evidence of its presence. On treatment with ammonium sulphide, the two bands appeared, intensified, as in the case of the pulmonate mollusca, by caustic soda. The first band alone was easily read; it extended from  $\lambda$  568.5—559.5. The presence of enterochlorophyll, on the other hand, could not be detected.

In the sub-kingdom, Echinodermata, certain starfishes and sea-urchins were examined. These yielded the usual five-banded spectrum of chlorophyll on addition of nitric acid to the alcoholic extract of the intestinal appendages.

The presence of these pigments, lutein and tetronerythrin, was likewise indicated in the course of the examination of specimens of starfish. The latter pigment was found in the integument, and had also been found in the shells of the crustaceans previously referred to.

The author concludes from these observations that the existence of



enterochlorophyll in the liver or other appendages of the intestine of the animals examined is definitely established. The bile of the pulmonate mollusca and of crayfish contains in addition hæmochromogen, which would appear to be a respiratory pigment, enabling intestinal respiration to be carried on, as in certain crabs, and *Cobitis fossilis*. The so-called liver of these invertebrates in addition to the preparation of a digestive ferment, discharges the function of a pigment-storing and pigment-producing organ in connection with surface coloration.

In some additional observations on the absorption-spectra of bile-pigments in vertebrate animals, the author alludes to his previously published observations, which appear to refer certain bands seen in bile to the presence of altered hæmatins (*Proc. Roy. Soc.*, **31**, 26). He has since proved that urobilin is absent in the bile of reptiles during hybernation. It was detected in the liver of *Salamandra maculata* in larger quantity than could be accounted for on the supposition of its presence in the blood-vessels of that organ, hence its probable formation there.

Concerning the origin of the colouring-matter of bile, proof of the transformation of hæmoglobin into biliverdin was afforded by a pathological fluid derived from the *tunica vaginalis testis* in a case of chronic epididymitis, when tapping had been previously resorted to for removal of the effusion. The fluid without any treatment showed the presence of a hæmoglobin derivative, and the pigment was proved by the action of oxidising and reducing agents to be biliverdin.

Experiments made on the colouring-matters of sheep- and ox-bile, although not completed, tend so far to show that chlorophyll as such cannot be present, inasmuch as the position of the band in red is altogether different, and the spectrum of acid chlorophyll was not obtained with nitric acid. Contrary to the statement of Hoppe-Seyler, the author, by direct experiment, finds that the pigments produced from bilirubin by oxidising agents and those of sheep- or ox-bile are not identical.

Referring next to urinary pigments, the author finds that febrile urobilin is not identical with hydrobilirubin or stercobilin, an alcoholic solution of the former, when acted on by caustic soda, yielding no bands at C and D, as in the case of similarly prepared solutions of the two latter. Harley's "urohæmatin" is shown to be a mixture of several decomposition-products of chromogens under the influence of heat and acids. The urohæmatin described by the author has been met with in four cases of acute rheumatism, and in a case of "idiopathic" pericarditis, its presence in the urine indicating insufficient oxidation of bodies with which it is associated, the normal oxidation of hæmoglobin to urobilin not taking place. Its occurrence in rheumatic fever would further seem to point to an acid fermentation, accompanied by destruction of hæmoglobin and production probably of lactic acid. The presence of urohæmatin in urine can be easily detected, without preliminary isolation, by its characteristic spectra, those of acid and neutral urohæmatin, which are distinguishable from those of methæmoglobin or hæmatin, by the use of ammonium sulphide, which does not affect urohæmatin.

*Spectroscopic Detection of Indican.*—Indican when present in the urine may be detected by its spectrum when Jaffe's test fails.

The urine, mixed with its own bulk of hydrochloric acid, is boiled, and after cooling, shaken, but not violently, with chloroform. The chloroform layer, if indican be present, is more or less violet, and shows a band before D, and generally one after it. It is noted that the reddening of normal urine when boiled with hydrochloric acid, is not due to the oxidation of indican, and only partly to the oxidation of urobilin chromogen. The author agrees with the view that this reddening is due to urobilin, and that this and indigo-red are two different colouring-matters. He has noticed a band half way between D and E, and extending nearly to E,  $\lambda$  558—534, in most cases in which indican has been detected by the method described; and treatment with reagents pointed to its being due to some other colouring matter, although in some way connected with the presence of indican.

Uroerythrin, obtained in alcoholic extract from pink urates, gives a double absorption-band of hazy outline from about three-fourths the distance between D and E to beyond F. No connection could be established between it and indican or urobilin. It often accompanies urohæmatin.

In conclusion, the author refers to the existence of a red colouring-matter in pale urine, which becomes visible on adding a mineral acid, but which, as its spectrum showed, is neither indigo-red nor urrhodin. It was also not due to the oxidation of the chromogen of urobilin. From lack of material, the study of this pigment had to be left incomplete.

D. P.

### **Albuminoïds of the Vitreous Humour of the Human Eye.**

By P. GIACOSA (*Gazzetta*, 13, 171).—In this liquid, the author has detected mucin, a globulin, and an albuminous substance analogous to serum albumin. Considering the small proportion of albuminoïds existing in this liquid, the author regards its viscosity as due to an excess of salts over the albuminoïds.

H. W.

### **Chemical Composition of the Egg and its Envelopes in the Common Frog.**

By P. GIACOSA (*Gazzetta*, 13, 171).—To isolate the envelope, the author placed the eggs for some hours in lime-water, whereupon the envelope dissolved, while the yolk settled down to the bottom. The filtered solution, treated with acetic acid of 10 per cent., yielded a flocculent precipitate, which, after repeated washing with acetic acid and with pure water, gave by analysis 52.71 per cent. C, 7.1 H, 9.33 N, 1.32 S, and 0.62 ash, whence the author infers the presence of a mucin. This substance resists putrefaction, and does not reduce copper salts till after boiling with dilute sulphuric acid. The author intends to study the products of this decomposition, but as he has not been able to detect the presence of any other bodies, he concludes that the enveloping membrane of frogs' eggs consists of pure mucin. From the oviduct of the frog he also succeeded in extracting a mucin, which, though differing from the

preceding in centesimal composition, nevertheless agrees with it in all other characters. H. W.

**Localisation of Arsenic in a Case of Poisoning.** By J. GUARESCHI (*Gazzetta*, 13, 176).—From the experiments of Scolosuboff, it would result that arsenic accumulates chiefly in the nervous system, whereas, according to Johnson and Chittenden (*Amer. Chem. J.*, 2, 332; Abstr., 1881, 1082), it is localised chiefly in the kidneys and liver, and according to Ludwig (*Schmidt's Jahrbücher*, 1881, p. 189), it accumulates chiefly in the liver, and is found also in the bones. The author, having carefully examined the viscera of an individual who died of arsenical poisoning, found that, out of 100 parts of arsenic, the stomach contained 0·0165, the liver 0·00105, the large intestine 0·00133, the lungs and heart 0·006, the muscles 0·0011, and the brain only traces, whence it appears that arsenic tends to accumulate chiefly in the liver, and is likewise found in notable quantity in the lungs and kidneys. H. W.

**Physiological Action of Paraldehyde and Contribution to the Study of Chloral Hydrate.** By V. CERCELLO (*Gazzetta*, 13, 172).—The action of this substance is hypnotic and similar to that of chloral, excepting that it does not diminish the pressure of the blood, unless administered in large doses. The sleep which it produces is calm, and not accompanied or followed by disturbances; in fact, it is similar to normal sleep. Paraldehyde is absorbed by the stomach, rectum, and subcutaneous tissue. The author supposes that it acts on the cerebral hemispheres, and then on the *medulla oblongata* and spinal marrow. He recommends it for medical use as an excellent substitute for chloral. H. W.

**Supposed Toxic Action of Aqueous Solutions obtained from Fresh Animal Organs.** By E. DI MATTEI (*Gazzetta*, 13, 172).—The author shows by numerous experiments that the symptoms of poisoning consequent on injection of the aqueous extracts of fresh organs (under the skin, into the veins, or into the peritoneal cavity) are due, not to any special toxic principle contained in these organs, as might be inferred from the experiments of Pellicani, but to a purely infective process, determined by the action and decomposition of insoluble but decomposed and alterable materials held in suspension by the injected liquids. In fact, when the turbid juice is freed from solid matters, either by filtration or by evaporation, and only the liquid portion is injected, death does not supervene. Another mode of experimenting consists in injecting beneath the skin of an animal the fresh juice of an organ reduced to a pulp, but not filtered, and, after a time more than sufficient to ensure the complete absorption of the liquid portion, making a wide incision in the skin at the point of injection, and washing with water containing phenol, in order to remove the solid matters remaining beneath the skin. Operating in this manner, death does not occur. H. W.

## Chemistry of Vegetable Physiology and Agriculture.

**Valuation of Seeds.** By A. MAYER and others (*Bied. Centr.*, 1883, 324—325).—Mayer employs as a germinator a glass flask 15 cm. high and 6 cm. broad, having an opening close to the bottom, which allows of the free circulation of air, and removal of excess water. The seeds are laid on blotting paper or cotton stuff placed inside the flask. When compared with Nobbe's germinator, it was found that Mayer's was best for clover, whilst Nobbe's was best for most grass seeds. The reports of germinative power of a sample are made thus:

(1) Value =  $\frac{\text{purity} \times \text{germinative power}}{100}$ ; (2) percentage of foreign

seeds, which are divided into harmful and harmless. As regards the influence of light, the author finds that the germination of *Poa pratensis* and *Dactylis glomerata* is accelerated, whilst the admission of air has no effect on *Pinus silvestris*, *Lolium perenne*, *Festuca ovina*, and *F. duriuscula*. Nobbe considers that germination should be tried in his germinator, on paper, in sand and in mould, before a satisfactory report can be made. A previous soaking for 6—12 hours is recommended for hard seeds, as also to remove the mucilage from the seeds of *Linum*, *Camelina*, *Cydonia*, &c., so as to admit oxygen more readily to the embryo.

E. W. P.

### Chemical Changes induced by the Sprouting of Grain.

By M. MÄRCKER and KOBUS (*Bied. Centr.*, 1883, 326—328).—The following table shows the changes which occurred when a sample of barley was exposed to bad weather for a fortnight; the rest of the crop had been well harvested. The ordinary analysis showed no difference between the samples; it was only when a more searching examination was made that a change was manifest:—

	Soluble starch.	Dextrin.	Dextrose.	Maltose.	Other soluble matter.	Total starch.	Nitrogen in dry matter.
Normal ...	1·76	1·1	0·0	3·12	5·64	64·10	1·90
Sprouted ..	1·17	0·0	4·92	7·32	5·23	57·98	2·045

	Nitrogen as nitrates.	Nitrogen as amide.	Nitrogen as ammonia.	Nitrogen as soluble albumin.	Nitrogen as insoluble albumin.
Normal .....	trace	0·028	0·045	0·087	1·740
Sprouted .....	trace	0·454	0·044	0·036	1·511

Kobus found that in wheat, under similar circumstances, the nitrogenous matter was most affected, the gluten being reduced by 20—25 per cent.

E. W. P.

**Function of Silica in the Vegetation of Maize.** By V. JODIN (*Compt. rend.*, 97, 344—346).—A grain of maize cultivated in a suitable solution of inorganic salts will develop and form a plant of normal appearance without assimilating any notable proportion of silica. This deprivation of silica produces no physiological degeneration in the plant, which can be cultivated in a similar manner through several generations. Under somewhat similar conditions a maize plant will develop and attain full maturity, although retaining in its tissues only one-quarter the normal amount of phosphoric acid and one-half the normal amount of potassium. By cultivating in well moistened vegetable soil, a grain from a plant of the fourth generation cultivated in water free from silica, a strong and vigorous plant is obtained which contains only one-sixth the normal amount of potassium.

These facts confirm Déhérain's supposition that the ash of a plant contains an amount of inorganic salts greatly in excess of that actually required for the proper development of the plant. The accumulation of this excess in the tissues of the plant is due to the purely physical forces, diffusion and evaporation.

C. H. B.

**Constant Production of Oxygen by the Action of Sunlight on "*Protococcus pluvialis*."** By T. L. PHIPSON (*Chem. News*, 48, 205—206).—In the summer *Zygnema* and *Conferva* may frequently be seen borne to the surface of pools of stagnant water by innumerable minute bubbles of oxygen-gas. Some of the simplest of the unicellular algæ, e.g., *Protococcus pluvialis* and *P. palustris*, exhibit this peculiarity to a remarkable degree. The author has cultivated some of the last-mentioned plants by exposing pump-water to air and light for some weeks, and, as soon as good growth was obtained, small dead branches of poplar were put in the water; the *protococcus* developed rapidly upon them. The branches can then be put in flasks full of water and the production of oxygen observed; this takes place immediately the flasks are exposed to the sun's rays; the oxygen comes off in the minutest bubbles, but in such great numbers as to form a froth on the surface; in some higher plants, e.g., *Achillea millefolium*, the gas collects at the ends of the leaves and comes to the surface in large bubbles. If the flask is inverted the evolution of gas continues for about three days; the introduction of a minute quantity of caustic soda stops it on the first day by depriving the plant of carbonic anhydride. On renewing the water, after three days, the evolution recommences, and so by keeping up a constant supply of pump-water, the production of oxygen may be kept up to all appearance indefinitely. The author has devised a simple apparatus for this purpose—a wide-mouthed bottle with tubulure near the bottom is fitted with a gas delivery tube and a tube with tap connected with a water supply; the water must neither be boiled nor distilled, nor must it be in the slightest degree alkaline. A tap is put in the

tubulure and is used to empty the bottle. Some of the working poplar branches are placed in the bottle, water is run in, and the bottle exposed to sunlight; the oxygen can be collected in a gas-holder. After three days the old water is run out of the bottle and fresh water run in. The author suggests that by employing graduated vessels, &c., the apparatus might be used as an *actinometer*. The gas produced contains about 98 per cent. oxygen. The author remarks incidentally that carbonic anhydride in presence of sunlight is not decomposed by plants, but simply absorbed, water and hydrogen dioxide being equally essential for the production of oxygen, and the gas being evolved from the tissue as a consequence of the absorption.

D. A. L.

**Aldehydic Nature of Protoplasm.** By A. B. GRIFFITHS (*Chem. News*, 48, 179—180).—After reference to the work of Loew and Bokorny (Abstr., 1882, 546, 447, and 882), of Reinke (*ibid.*, 243 and 1312), of Mori (*Chem. Centr.* [3], 13, 565), of Beyer, of Kretzschmar (*Bied. Centr.*, 1882, 830), and to his own communication to this Journal (Trans., 1883, 195), the author proceeds to describe his new experiments. He has examined the protoplasm of living and dead cells of *Spirogyra*, and finds that it reduces alkaline solutions of cupric salts; that crystals are formed in it by treatment with weak sodium chloride, and that the addition of absolute alcohol to the cells of the *Spirogyra* causes the deposition of crystals of anhydrous dextrose. It is therefore probable that the reducing properties of protoplasm are due to this glucose, and that the crystals formed with sodium chloride are  $C_6H_{12}O_6 \cdot NaCl + H_2O$ . This view is supported by the following experiments:—Albumin (white of fresh egg) mixed with a small quantity of a very dilute solution of dextrose, when treated as above described, behaves in a manner precisely similar to the *spirogyra* cells. Moreover, if the living plant is kept in the dark for a couple of days and is then examined, none of these reactions are observed. This is evidently due to the dextrose being used up in the dark to nourish the cell-walls and tissues, for after a short exposure to sunlight the dextrose reappears and the usual phenomena are to be observed in the plant cells. The author concludes with some remarks on the aldehydic nature of dextrose, on the assimilation of carbon by plants, and on the importance of researches on albumin.

D. A. L.

**Fatty Constituents of Common Chestnuts.** By P. MALERBA (*Gazzetta*, 13, 173).—Dry chestnuts contain at least 3 per cent. of fatty matters, for the most part liquid and of oily aspect, while the smaller portion is solid, the proportion of fatty matter increasing with age, and fatty acids being formed at the same time.

H. W.

**Cocoa and Chocolate.** By BOUSSINGAULT (*Ann. Chim. Phys.* [5], 28, 433—456).—The cacao plant rarely flowers before it is 30 months old, but the first flowers are generally destroyed, as the planters do not permit the plants to bear fruit before they are four years old; 100 kilos. of fresh fruit yield from 45 to 50 kilos. of dry cocoa. In Venezuela, after a plant is seven years old, it yields 0.75 kilo. annually. In Magdalena a tree yields 2 kilos. of dry cocoa per annum. The

kernel of the species *Montaraz* contains: Butter, 53·3; albumin, 12·9; theobromine, 2·4; gum and tartaric acid, 6·7; cellulose, lignose, starch, 9·1; ash, 4·0; water, 11·6 per cent. The ash consists chiefly of phosphate of calcium, magnesium, and potassium; it also contains silica, carbonic and sulphuric acids. The husk has the following percentage composition:—Butter, 3·9; nitrogenous matter, 14·25, containing 2·8 N; gum, 12·12; tartaric acid and tannin, 5·05; ash, 6·89; water, 12·18; lignose, cellulose, and other compounds not estimated, 45·61. The process of decortication is generally accomplished by means of gentle heat. The following table shows the composition of Trinidad cocoa, decorticated A by heat, B without heating:—

	A.	B.
Butter .....	54·0	49·9
Starch and glucose ..	2·5	2·4
Theobromine.....	3·6	3·3
Asparagine .....	trace	trace
Albumin .....	11·8	10·9
Gum .....	2·5	2·4
Tartaric acid.....	3·7	3·4
Tannin .....	0·2	0·2
Soluble cellulose ....	11·5	10·6
Ash .....	4·4	4·0
Water .....	—	7·6
Not estimated .....	5·8	5·3

Cocoa butter is a white solid which melts at 30° and solidifies at 23°. The gum resembles gum arabic in appearance, and also yields mucic acid when treated with nitric acid. It is powerfully dextrogyrate. Chocolate, prepared by grinding together sugar and gently roasted cocoa, contains varying amounts of sugar. Spanish chocolate contains from 40·6 to 54 per cent. of sugar, and French chocolate contains from 56 to 59 per cent.

The relative value of chocolate and milk as food is seen from the following analysis of equal weights of milk and an emulsion containing 20 per cent. of chocolate:—

	Chocolate emulsion.	Milk.
Albumin .....	3·0	13·6
Fats .....	14·0	15·0
Sugar.....	32·0	15·0
Salts .....	1·0	2·7

The large proportion of sugar in chocolate diminishes its nutritive power.

W. C. W.

**Analysis of some Cider Apples.** By R. LEZÉ (*Ann. Agronomiques*, 9, 105).—The fruits were exhibited at the Apple Congress of St. Lô, November, 1882, and analysed by the author at the end of December:—

Variety.	Water.	Sugar.	Ash.	Tannin.	Cellulose, albuminoids, &c.
Haut griset.....	80·96	7·64	0·52	0·50	10·38
Avoine.....	83·38	9·19	0·37	0·21	6·85
Doux lozon. ....	80·64	9·22	0·36	0·19	9·59
Aufrique tardive .....	82·02	8·59	0·46	0·35	8·58
Cartigny gros.....	81·08	10·41	0·34	0·57	7·60
Fréquin.....	84·02	6·08	0·28	0·72	8·90
Airu.....	83·90	8·50	0·36	0·23	7·01
Petit rouget .....	84·90	7·40	0·32	0·27	7·11

The variety Fréquin is well known as yielding good cider, which will keep well.  
J. M. H. M.

**Poisonous Properties of Edible Fungi.** By G. DUPETIT (*Bied. Centr.*, 1883, 356).—The physiological action of the juices of many fungi on animals is detailed in this paper. The poisonous principle is soluble in water, but insoluble in ether, chloroform, carbon bisulphide, and alcohol; it is precipitated from its solutions by alcohol, tannin, lead acetate, and hydroxide; it therefore less resembles the alkaloids than the soluble ferments, and its action is destroyed at 100°. In *Boletus* two non-poisonous alkaloids have been found, the one resembling neurine, the other the ptomaines.  
E. W. P.

**Report on Experimental Plots at Grignon in 1882.** By P. P. DÉHÉRAIN (*Ann. Agronomiques*, 9, 106—124).—The crops grown in 1882 were wheat, oats, green maize, sugar-beet, and sainfoin. The yield of oats was under average, and that of wheat very poor, 35 hectolitres per hectare against 50 harvested in 1880. The author attributes the difference, not to the rainfall, which was less and more equally distributed in 1882 than in 1880, but to the difference in temperature, the monthly mean from March to September being from 1·3° to 5·6° (July) less in 1882 than in 1880. For the same reason the vintage of 1882 was a bad one, as the grapes never ripened perfectly.

*Wheat.*—All the plots carried potatoes from 1875—1879, and wheat 1880—1882; since 1879 no nitrogenous manure has been used. The best yield (27—30 hectolitres) was on those plots which had received dressings of farmyard manure from 1875—1879; plots dressed with sodium nitrate during the same period gave no more grain than the plot unmanured since 1875, although the straw was slightly heavier; and plots which received ammonium sulphate, 1875—1877, yielded less of both grain and straw than the plot unmanured since 1875. The entire wheat crop of the neighbourhood suffered much from rust in June; 10 grams of wheat from one of the plots contained 128 well developed grains weighing 6·12 grams, and 132 stunted badly filled grains weighing 3·88 grams. The two lots were analysed and found to be almost identical in composition.

*Oats.*—The harvest from the experimental plots was worse than the



average of the four years 1878—1881, but better than 1881; the deficiency was most marked in the grain, and the author attributes the falling off to the difficulty of cleaning land carrying the same cereal crop so many years in succession. Oats have been grown on all the plots for the last eight years, and in 1882 the yield from most of the manured plots was actually less than that on the two plots receiving no manure, owing to the encouragement afforded by the manures to the growth of weeds.

*Green Maize.*—The seventh consecutive year of this crop has yielded results similar to those of the preceding years. The yield, favoured by a wet season, has shown no falling off, and farmyard manure in quantities up to 29,000 kilos. per hectare, has proved by far the most efficacious and remunerative dressing; with 40,000 kilos. instead of 20,000, the increased yield is not sufficient to cover the extra cost of the manure. A moderate dressing of farmyard manure each year has given better aggregate results than the same total quantity distributed over the three years 1875—1877. Partial or complete substitution of sodium nitrate for farmyard manure has resulted in diminished crops.

*Sugar-beet.*—This crop has been grown in 1881 and 1882 on six plots which carried green maize for the six previous years; the previous dressings on half the plots having been farmyard manure, and on the others ammonium sulphate. The results of 1881 were so decidedly worse on the ammonium sulphate plots, that in 1882 an attempt was made to restore their fertility by new dressings of farmyard manure alone or with artificials: 20,000 kilos. farmyard manure, together with 200 kilos. each of sodium nitrate, superphosphate, and potassium chloride, was the only application which raised the produce of the ammonium sulphate plots to a level with the plots which received no manure in 1881 or 1882, but had been dressed with farmyard manure in 1878, '79, '80. The sugar in average samples of roots from each plot was determined by the polariscope, the percentage varying from 12·04 to 13·73 (the variety grown was *Vilmorin's betterave au collet rose*). The results confirm the author's previous conclusions that the richness in sugar is lowered by nitrogenous manures, and is not sensibly raised either by potassium salts or superphosphate. The most remarkable fact in this series of experiments is the decreased crops on the plots which formerly received ammonium sulphate, a result which the author attributes to the injurious action of this salt on the physical properties of the soil.

*Sainfoin.*—The sainfoin grown in 1879 had become replaced by grasses at the end of 1881; a new sowing was therefore made in 1882, and a satisfactory crop obtained, the best plots being those which were heavily dressed with farmyard manure from 1875—1878. Analyses of the soil and subsoil, made in the four years preceding 1879, during which the plots carried sugar-beet and green maize, showed a slight progressive diminution in the percentage of nitrogen, even in those plots which received large dressings of farmyard manure; since the occupation of the ground by sainfoin, however, the percentage of nitrogen has remained stationary or has slightly increased. No figures are given on this point. J. M. H. M.

**Influence of Rainfall on the Wheat Crop.** (*Bied. Centr.*, 1883, 291—294).—A table of the rainfall and temperature in England during July and August, in the years 1846—1876, is given, and this is divided into four groups; comparing this table with the wheat crops, it appears that when the average temperature of July and August is above the mean, the crop is above average: rain during warm seasons does not lower the quantity although the quality may be deteriorated; however good a season may be in June, no good crop is obtained—that is one above the average—if the average temperature in July and August is below the mean; even if the weather in those months be fine, the quality only is good. If during July and August there is both wet and cold, the yield is always low and the quality poor.  
E. W. P.

**Comparative Feeding Value of Barley, Malt, and Peas.** By A. VOELCKER (*Jour. Roy. Agri. Soc.*, 1883, 422).—These experiments were conducted at Woburn. The barley and malt were used in the proportion shown in the malting operation, 140 lbs. of barley yielding 117 lbs. of malt and malt-dust. Three pens, each of ten sheep (10 months old), received throughout the same quantity of swedes, with hay and straw chaff. During the first period of eight weeks, each sheep had in addition  $\frac{1}{4}$  lb. of linseed cake per day; pen 1,  $\frac{1}{4}$  lb. of barley meal; pen 2, the equivalent in malt-meal and malt-dust; pen 3,  $\frac{1}{4}$  lb. of pea-meal. In the second period of two weeks the additional foods were increased to  $\frac{1}{2}$  lb. per head per day. In the third period of two weeks they were raised to  $\frac{3}{4}$  lb. In the fourth period of two weeks they were raised to 1 lb. The gain in live-weight of the sheep of each pen was as follows:—

	Pen I. Barley.	Pen II. Malt.	Pen III. Peas.
	lbs.	lbs.	lbs.
First eight weeks.....	200 $\frac{1}{2}$	227 $\frac{3}{4}$	228 $\frac{3}{4}$
Following six weeks....	93	73 $\frac{3}{4}$	113
Total fourteen weeks....	293 $\frac{1}{2}$	301 $\frac{1}{2}$	341 $\frac{3}{4}$

The feeding values of the barley, and of its equivalent in malt, were thus practically equal, whilst that of the peas was distinctly greater.

The maximum rations were continued for two weeks longer; during this time the sheep of pen 1 refused a part of their barley, the results therefore ceased to be comparative.  
R. W.

**Composition and Digestibility of Serradella at various Ages.** By H. WEISKE, G. KENNEPOHL, and B. SCHULZE (*Bied. Centr.*, 1883, 307—309).—The seed was sown in the middle of April on two plots, from the first of which a crop was taken on July 22, and from the latter on October 2, also an aftermath was taken from the first plot on October 2. The composition of the crops was as follows:—

	Plot 1.		Plot 2.
	July 22.	October 2.	October 2.
Yield—			
Fresh.....	110·0 kilos.	4·345 kilos.	85·00 kilos.
Dry .....	13·83 „	0·577 „	17·15 „
Containing—			
Albumin.....	22·62 p.c.	24·75 p.c.	19·13 p.c.
Fat, &c. ....	5·2 „	5·12 „	3·95 „
Fibre.....	29·65 „	27·11 „	35·71 „
Cellulose, &c.....	30·89 „	34·33 „	32·39 „
Ash .....	11·64 „	8·69 „	8·82 „

Feeding experiments showed that the younger plant was more easily digested than the older. E. W. P.

**Analyses of Heather (*Erica vulgaris*), Braken (*Pteris aquilina*), and Broom (*Genista pilosa*).** By A. PETERMANN (*Ann. Agronomiques*, 9, 251—255).—Vast tracts of poor soil in the Ardennes (derived from schists and quartzose schists) are covered with a thick vegetation of heather, broom, and fern, which is useful to the inhabitants in many ways. The dense mass of vegetation assists in the disintegration of the rock, and acts as a sponge in storing up and gradually giving out the rainfall. Sheep and horses readily eat the young shoots of broom and heather, and the ashes of these plants, burnt on the spot, are found to be a good manure for oats. Cut with the scythe, air-dried, and stacked, these plants furnish fuel in the winter and litter for cattle.\* Sometimes they are ploughed in as green manure, and frequently broom in flower is made into a compost with soil and refuse. The analyses in the subjoined tables were made on the air-dried plants, including stems, leaves, and flowers:—

	Fern.	Heather.	Broom.
Water.....	14·70	12·70	12·30
†Organic matter .....	75·75	85·06	84·79
Mineral matter .....	9·55	2·24	2·91
	100·00	100·00	100·00
†Containing nitrogen .....	2·38	0·80	2·54

\* Fern litter is also extensively used in the New Forest.—J. M. H. M.

*Composition of the Ash after Deducting Carbon, Sand, and Carbonic Anhydride.*

	Fern.	Heather.	Broom.
Potash.....	38·53	31·74	43·28
Soda .....	3·31	5·98	4·18
Lime .....	11·69	19·78	18·57
Magnesia .....	6·93	13·28	10·05
Oxide of iron .....	0·91	3·06	1·12
Sulphur trioxide .....	7·93	8·14	4·61
Phosphorus pentoxide .....	4·60	2·73	14·05
Silica .....	17·51	13·47	1·11
Chlorine .....	11·09	2·35	3·89
Manganese .....	—	trace	trace
	102·50	100·53	100·88
Deduct oxygen equivalent to chlorine ...	2·50	0·53	0·88
	100·00	100·00	100·00

Fern and broom thus contain six times, and heather twice as much nitrogen as rye-straw, and their ashes are rich in phosphoric acid and potash.  
J. M. H. M.

**Beet Cultivation.** By CRAHÉ and others (*Bied. Centr.*, 1883, 333).—Crahé found on large plots that a mixture of Chili saltpetre and Baker guano was a more productive manure than ammonium sulphate and guano, both as regards yield of root and of sugar. Märcker found that in 1880 Simon le Grand Rose was the best cropper but lowest yielder of sugar, but in 1881 Klein Wanzlebene was the highest cropper and Vilmorin Blanche gave the best yield of sugar.

E. W. P.

**Potatoes and Sweet Potatoes.** By SACC (*Bied. Centr.*, 1883, 337).—Potatoes which are planted at all seasons of the year, as in Monte Video, are watery and tasteless, and have the composition—albumin 0·71—0·81, dextrin 0·02—0·05, sugar 1·3, starch 10·2—12·81, bitter extract 2·25, fibre 13·18—11·59, calcium bimalate 0·05, water 73·59—72·91, but if they are planted in October then the composition is normal. Sweet potatoes (*Convolvulus batatas*) require more heat, and contain—albumin 0·56—0·64, glucose 4·0—0·3, mucilage 1·15, pectic acid 1·27, starch 15·0—13·01, fibre 10·02—17·83, ash 1, water 67·0—68·19. They require an open soil and but little manuring. The sweet potato is finer than the potato, and is quite as useful, being largely used in the manufacture of spirits.

E. W. P.

**Assimilation of the Organic Matter of Arable Soil.** Part I. Historical Résumé. By P. P. DÉHÉRAIN (*Ann. Agronomiques*, 9, 258—265).—The idea that plants directly assimilate the organic matter of the soil was supported by de Saussure, Malaguti, and Soubeyran, and opposed by Liebig and Boussingault. The last-named chemist contended that the utility of humus to vegetation consists in

the continuous disengagement of large quantities of carbonic anhydride in the soil, and subsequent writers have supposed that this carbonic anhydride is absorbed by the roots, conveyed to the leaves, and there decomposed in presence of chlorophyll and sunlight. No evidence in favour of the absorption of carbonic anhydride by roots could be obtained by Corenwinder from direct experiments on the point; on the contrary, he has shown that roots take part in respiration, absorbing oxygen and emitting a little carbonic anhydride. Grandean has attributed another function to humus. He found that the ammonium carbonate extract of soil contains, besides the brown humus bodies, considerable quantities of phosphoric acid, oxide of iron, magnesia, lime, and soluble silica. When this solution is dialysed, only the mineral constituents pass through the septum, forming a colourless solution, the brown matter left on the septum containing only 8 per cent. of ash, whereas before dialysis it contains 53 per cent. From these experiments Grandean concludes—(1) that the minerals combined with humus are directly assimilable by the roots of plants; (2) that the organic matter itself does not enter the roots, but is the vehicle of the mineral aliment; (3) that the combination of minerals with humus is similar to that found in the liquor of a dung-heap; and (4) that the fertility of a soil is proportional to the quantity of minerals associated with humus and soluble in ammonium carbonate. Petermann has recently demonstrated (and his experiments have been repeated by Grandean) that soil *not* treated with ammonium carbonate does contain dialysable organic matter, and the question remains, does this organic matter serve directly as plant food? The author's observations on the experimental maize plots at Grignon render an affirmative reply probable. The plots dressed each year with 40,000 kilos. farmyard manure have given an average annual yield of 90,000 kilos. green maize, whilst the highest yield obtained by the use of chemical manures is 68,000 kilos. When maize is grown with the aid of farmyard manure, the soil is found to be much more impoverished of carbon than in the case of potatoes or wheat, which do not benefit so much from the same manure. The author finally quotes the opinion of Sachs, who, after noting the direct assimilation of organic matter by fungi, germinating seeds, and certain parasites, considers it probable that green plants also may share in this function. The direct experiments of the author will be given in a future number.

J. M. H. M.

**Ammonia, Chlorine, and Sulphuric Acid in Rain collected at Rothamsted.** By Sir J. B. LAWES, J. H. GILBERT, and R. WARINGTON (*Jour. Roy. Agri. Soc.*, 1883, 313).—The results of earlier determinations have been given in a previous paper (Abstr., 1882, 889).

1. *Ammonia in Rain.*—The new determinations were made both in daily rainfalls and in monthly mixtures. The rain was distilled, and the distillate Nesslerised. In 152 daily collections of rain, dew, &c., in the large rain-gauge (0.001 acre), extending from June 22, 1881, to January 5, 1882, the nitrogen as ammonia varied from 0.043 per million (in a rainfall of 0.713 inch on Nov. 27) to 5.49 per million (in a deposit of dew of 0.007 inch on September 17). The rainfall during the whole period amounted to 21.645 inches, and contained an average

of 0.254 of nitrogen as ammonia per million. The proportion of ammonia is much greater in small deposits than in large; it is affected to a still greater extent by the amount of previous washing which the atmosphere has undergone. Ammonia was also determined in 50 monthly mixtures of rain-water. In 24 recent months the analysis of the water was made at the end of each month; the earlier monthly samples were in most cases of considerable age when analysed. In the 24 recent samples the nitrogen as ammonia averaged 0.316 per million; in the whole series of 50 months the average was 0.361. Evidence is given showing that the ammonia in the rain-water generally tended to increase by keeping. Nitrification was possibly prevented by the lead present in the water. The rainfall of summer was generally richer in ammonia than that of winter. The nitrogen as ammonia contributed annually by rain to an acre of land amounts to 2.37 lbs. if calculated from the daily determinations during six months, to 2.47 lbs. calculated from two years' determinations in fresh monthly mixtures, and to 2.66 lbs. if calculated from determinations in 50 monthly mixtures, many of them old. From the last series of determinations it appears that to double the quantity of ammonia per acre the rainfall must be increased about six-fold. From Frankland and Way's results, the nitrogen as nitric acid appears to be about 1 lb. per acre, and the nitrogen as organic matter a similar amount. The total combined nitrogen in the annual rainfall at Rothamsted is thus about 4.5 lbs. per acre.

2. *Chlorine in Rain.*—The determinations of chlorine in monthly mixtures of rain extend over six years, 1877—83. The mean proportion found was 1.99 per million of water, or 14.92 lbs. per acre, equal to 24.59 lbs. of sodium chloride. Two-thirds of the chlorides fall in the six winter months, October to March. The minimum quantity falls in July, the maximum in October and November. The supply of chlorides in summer seems to be very limited, as a large increase in the rainfall produces but little increase in the quantity of chlorides per acre. In winter the increase in the quantity of chlorides with a rise in the rainfall is much greater.

3. *Sulphuric Acid in Rain.*—The sulphuric acid was determined gravimetrically in mixtures representing the rainfall of summer (April—September) and winter (October—March); the determinations extended over two years. When the rain was collected in glass vessels only, the average amount of sulphuric anhydride was 2.41 per million of rain or 18.5 lbs. per acre. When the rain was collected in the large rain-gauge the amount of sulphuric anhydride was 3.95 per million, or 30.3 lbs. per acre. There seems little doubt that in this latter case a part of the sulphuric acid was derived from the vulcanised caoutchouc used for the connections. The rain appears to be slightly richer in sulphuric acid in summer than in winter.

R. W.

**Influence of Artificial Manures on the Physical Properties of Soil.** By E. WOLLNY (*Ann. Agronomiques*, 9, 129—131; from *Zeits. des Vereins für die Rübenzuckerindustrie*, November, 1882).—The addition of small quantities of ammonia or fixed alkalis, or of alkaline phosphates or carbonates to water holding clay in suspension, causes

the immediate precipitation of the clay in a dense form. Mineral acids and their salts, such as sodium nitrate, act in the opposite manner, precipitating the clay in a light and spongy form, which occupies much space. Hence the author argues that the addition of substances of the former class to soils is injurious to their porosity and lightness, and consequently to fertility, and cites as examples the alkali plains of Nevada and California, the soil of which is hard, dense, non-porous, and sterile. On the other hand, salts such as sodium nitrate, saltpetre, and potassium sulphate exercise an immediate beneficial effect on the porosity of arable soil, but as they are quickly washed out the effect is not lasting, and the fertility is then found to be impaired. Of all artificial manures, lime exercises the most favourable influence on the properties of soil, causing it to aggregate into flocculent particles which persist for years, and render it light and fertile.

J. M. H. M.

**Weeds in Soils.** By H. PUTENSEN (*Bied. Centr.*, 1883, 295—297).—In this paper it is shown that repeated ploughings and harrowings diminish the number of weeds in the soil.

E. W. P.

**Manuring Experiments at Kiel.** By A. EMMERLING (*Bied. Centr.*, 1883, 297—306).—This is a report of the experiments made in 1881, which are a continuation of those conducted in 1880; the season was bad, yet conclusions may be drawn which are not without interest, as showing the action of artificial manures under unfavourable circumstances. There were 24 sets of plots on various soils, the crops being generally oats, but buckwheat, barley, and beans were also grown. The manures were superphosphate, precipitated phosphate, dissolved and raw Peruvian guano, steamed and dissolved bone-meal, blood, ammonium salts, and Chili saltpetre (86·9 per cent.). The results are given in full detail in a series of tables. A short summary of these is given here. Ammonia acted but feebly on clay loam, and not at all on sand, but well on black humus earth. Saltpetre was satisfactory in all classes. Phosphates with ammonia produced a low yield in that district where the weather was unpropitious. Phosphates and saltpetre gave contradictory results owing to bad weather. Steamed bones raised the yield of grain, and especially at the drier stations; whilst steamed bones are best on dry lands, the dissolved meal best acted at those stations where rain had fallen in June. Blood failed at all the dry places. In spite of the unfavourable conditions, the guano (raw and dissolved) greatly increased the crop; the latter had, however, increased the grain and straw more than the former.

E. W. P.

**Manurial Value of Nitrogenous Refuse. IV. Dried Blood.** By A. PETERMANN (*Ann. Agronomiques*, 9, 241—251).—Thirty-two samples of dried blood examined in 1880—81 gave an average of 11·23 per cent. nitrogen; the physical condition also was satisfactory, being dry, friable, pulverulent, and almost without odour. The manurial value was determined by experiments on plants grown in pots, in two soils of very different physical characters, and the results were compared on the one hand with those obtained without manure,

and on the other hand with those obtained by using a quantity of sodium nitrate equivalent in nitrogen to the dried blood. The effect of adding phosphoric acid and potash to the dried blood was also studied. The results given in this abstract are in all cases the mean of two or three concordant experiments.

The first series consisted of 15 flower-pots filled with loamy soil from Gembloux mixed with a quarter of its bulk of quartz sand; the second, 15 pots filled with sand from Campine. Ten grains of spring wheat were sown in each pot on March 17th, 1882; on August 20th, 1882, the plants were removed from the pots, and the straw and grain weighed separately; the results are given in the table.

Manure.	Loam. Mean weight of		Sand. Mean weight of	
	Straw.	Grain.	Straw.	Grain.
No manure .....	18·19	7·94	5·35	2·08
Dried blood = 0·25 gram N .....	42·51	19·56	10·70	5·05
Sodium nitrate = 0·25 gram N .....	44·25	20·14	19·51	7·51
Dried blood (= 0·25 gram N) + precipitated phosphate (= 0·30 gram $P_2O_5$ ) .....	42·90	19·51	20·46	8·94
Sodium nitrate (= 0·25 gram N) + precipitated phosphate (= 0·30 gram $P_2O_5$ ) .....	44·96	19·62	21·36	9·76
Dried blood (= 0·25 gram N) + precipitated phosphate (= 0·30 gram $P_2O_5$ ) + potassium chloride (= 0·20 gram $K_2O$ ) .....	43·73	19·44	22·59	12·19
Sodium nitrate (= 0·25 gram N) + precipitated phosphate (= 0·30 gram $P_2O_5$ ) + potassium chloride (= 0·20 gram $K_2O$ ) .....	45·01	19·80	23·99	12·98

The highest yields are obtained in the loam, but the effect of the manures is greatest in the sand. In the loam, dried blood produces an increase in the crop practically identical with that given by a quantity of sodium nitrate containing the same amount of nitrogen; the addition of phosphoric acid, or potash, or both, has little effect. In the sand, on the contrary, dried blood is decidedly inferior to its equivalent of sodium nitrate, and both phosphoric acid and potash produce considerable effect; the effect of the phosphatic manure, in all the pots in which it was used, was to hasten the period of ripening.

As the result of these and previous experiments, the author arranges the nitrogenous manures which he has tried in the following order of efficiency (such quantities being employed as contain equal weights of nitrogen):—Sodium nitrate, dried blood, dissolved wool, wool refuse, leather refuse. The efficiency is plainly related to the solubility and readiness to decompose in each case.

J. M. H. M.

**Preparation of Manure from Furnace Slag.** By WINKELHOFER (*Bied. Centr.*, 1883, 354).—The excess of lime in the slag obtained in the “basic process” is to be removed by treatment with



molasses and water, which leaves the phosphates undissolved; the lime is then separated from the saccharate by passing the products of combustion from the furnaces through the solution.

E. W. P.

**Insoluble Phosphates.** By F. J. LLOYD (*Chem. News*, **48**, 164—165).—The “insoluble phosphates” from superphosphates are divided into two classes, the “white” and the “red.” The white are obtained only from manures made from bones, and represent approximately the amount of phosphate not dissolved.

The author has analysed the “red” phosphate with the following result:—

CaO.	Fe <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .
32·53	31·80	35·77 per cent.

These numbers correspond with 60·01 per cent. calcium phosphate, 17·63 per cent. ferric phosphate, 22·46 per cent. ferric oxide.

D. A. L.

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## Analytical Chemistry.

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**Volumetric Analysis.** By E. REICHARDT (*Arch. Pharm.* [3], 21, 106—115).—This paper contains instructions for the performance of the ordinary operations in volumetric analysis, including the precautions to be observed in the preparation of standard solutions, &c.

W. R. D.

**Determination of the Density of Solids and Liquids by means of the Specific Gravity Bottle.** By S. PAGLIANI (*Gazzetta*, 13, 172).—The author points out, as a source of error in these determinations, the fact that flat-bottomed glass bottles when filled with liquid exhibit very sensible alterations of level, even when only a slight pressure is exerted on the bottom; and in endeavouring to determine the capacity at 0° of one of these vessels, he observed that the level of the liquid contained in it at 0° was higher than at the ordinary temperature. He therefore recommends for liquids the use of the bottles described by Regnault (*Ann. Chim. Phys.* [3], 9, 438); and in cases when it is necessary to use the ordinary bottles, as in determining the densities of solid bodies, he suggests a previous examination, with the view of ascertaining whether they exhibit the defect above mentioned.

H. W.

**Apparatus for the Rapid Analysis of Gases.** By A. A. BRENNEMAN (*Chem. News*, 48, 156).—The apparatus consists of a eudiometer fitted with a soft india-rubber stopper bored with two holes, through which pass two tubes closed by valves; one is connected with an exhausted receiver, whilst the other has simply a pointed glass

tube attached to it. When in use the gas is introduced into the eudiometer over a pneumatic trough, and the volume read off in a convenient cylinder sufficiently full of water. The eudiometer is re-transferred to the trough of water, the stopper inserted, and most of the water drawn from the interior of the eudiometer by opening the valve in connection with the exhaust chamber; the absorbent is introduced by applying the point of the pipette to the pointed tube and opening the valve connected with it, when the liquid rushes in to replace the water which has been withdrawn. The absorption being complete, the liquid is removed by opening the exhaust valve (by which means all subsequent absorbents and washings are removed), the eudiometer well rinsed with water, and the volume again read off in the cylinder of water. The mouth of the burette is kept below the surface of water as much as possible. A special form of cup, with a long bent-up handle, is used for transferring the eudiometer from the trough to the cylinder, and *vice versa*. D. A. L.

**Apparatus for the Rapid Analysis of Gas.** By A. H. ELLIOT (*Chem. News*, 48, 189—191).—This apparatus consists of two glass tubes of the same length; one graduated from the top to within a short distance from the bottom, in tenths c.c. to 100 c.c.; the other plain. Both are connected at the lower end with two distinct reservoirs of water by means of flexible tubing; there is a three-way cock at the bottom of the plain tube, with one delivery through the stem. The top of the graduated tube terminates in a capillary tube, bent at a right angle, and fitted with a stopcock. At the top of the plain tube there is a straight capillary tube fitted with a stopcock, below which a lateral capillary tube is fused, which is joined to the capillary of the graduated tube by a rubber connection. Above the stopcock the operator can attach either a movable cylindrical funnel which is ground to fit over the tube, or the tube for the admission of the gas to be analysed. In use, the tubes are filled with water by opening the stopcocks in a suitable manner, and the plain tube is charged with gas, lowering or raising the water reservoirs; the gas is then transferred to and adjusted in the graduated tube, the volume is read off, and the absorbent having been run in to the plain tube through the funnel, the gas is retransferred to the last-mentioned tube, &c. In washing out the plain tube, use is made of the three-way cock; by bringing it into connection with the inside of the tube, and allowing the washings to run out. Absorbents are used in the following order—potash, bromine, potassium pyrogallate, and cuprous chloride. A special arrangement is employed for explosions: a stout glass tube is graduated in tenths c.c. and of 100 c.c. capacity to within a few inches from the bottom; the lower end is connected with a water reservoir, and has a lateral tube fused in the side and fitted with a stopcock; the upper end is closed by a capillary tube and stopcock (to which either a funnel or a piece of bent capillary tubing can be attached), and has platinum wires fused in through the glass. To use this, the tube is filled with water, and by means of the bent tube and india-rubber connections and the water reservoirs and stopcocks, a sufficient amount of gas is admitted from the absorption-tube, the

level adjusted, the volume read, and the oxygen allowed to enter by the lateral tube at the bottom, the explosion is proceeded with as soon as the gases have been mixed by slight agitation: the analysis is then finished in the usual manner, absorbents being run in through the funnel. After some practice, a complete gas analysis, using both absorption and explosion tubes, can be made in less than an hour, and results are obtained within a few tenths of a per cent. of the truth.

D. A. L.

**Estimation of Bromine in Presence of Large Quantities of Chlorides.** By A. CAVAZZI (*Gazzetta*, 13, 174).—The author's method consists in the use of oxygenated water ( $\text{BaO}_2$  and dilute sulphuric acid), which at  $100^\circ$  liberates all the bromine without decomposing the chlorides. The bromine-vapour is passed into a solution of arsenious acid in hydrochloric acid (0.10 g.  $\text{As}_2\text{O}_3$  in 20 c.c. of liquid) which absorbs it rapidly. To determine the quantity of bromine thus absorbed, a solution of potassium permanganate is prepared containing 3.55 g.  $\text{KMnO}_4$  in a litre of distilled water. Now the author finds that 18.30 c.c. of such a solution is just sufficient to impart a permanent red or yellow tint to 20 c.c. of the arsenical solution; and hence by a simple calculation, it is found that 1 c.c. of the same permanganate solution is equivalent to 0.00888 gram of bromine.

If iodides are also present, the iodine must first be separated by means of an acetic solution of barium dioxide and carbon bisulphide (as described by the author in another place), after which the solution containing the bromides and chlorides is mixed with pure lime to alkaline reaction, then evaporated to dryness, and the residue is calcined to convert the acetates of barium and calcium into carbonates. Lastly, the residue is treated with boiling water, and the bromine is determined by the method above described.

H. W.

**Purification of Hydrogen Sulphide.** By W. LENZ (*Chem. News*, 48, 147).—It is very important that all arsenic should be removed from the hydrogen sulphide employed in chemico-judicial investigations, and the author suggests the following process with this object. Four consecutive wash-bottles kept at a temperature of  $60-70^\circ$  are used to purify the gas. The first bottle contains a mixture of 1 part strong hydrochloric acid with 2 of water; the second, a solution of 1 part of this mixture to 4 of water; the third a similar solution containing 1 to 8; in the fourth, pure water. Neither caoutchouc stoppers nor vulcanised india-rubber connections are permissible. This washing system is very efficient.

D. A. L.

**Testing for Free Sulphuric Acid in Wines and Vinegar.** By E. POLLACCI (*Gazzetta*, 13, 315—316).—The author states that neither Nessler's method nor Lessaigne's gives satisfactory results, and proposes the following:—Strips of filtering-paper, purified by treatment with hydrochloric acid and washing, are immersed in a beaker containing the wine, so that they adhere to the sides, one end touching the bottom and the other projecting about a centimeter above the top, a sufficient number of strips being used to line the interior of the

vessel. After 24 to 36 hours, by the spontaneous evaporation of the liquid, a sufficient quantity of the acid will have accumulated in the upper extremities of the strips of paper; these are now cut off and repeatedly triturated with ether in a glass mortar. The ether is evaporated, the residue taken up by water and tested for sulphuric acid in the usual way. This method has the advantage that the free acid alone is separated and detected.

C. E. G.

**Direct Estimation of Carbonic Anhydride in Presence of Sulphides, Sulphites, and Thiosulphates of the Alkali-metals.** By M. KÖNIG and E. ZATZEK (*Monatsh. Chem.*, **4**, 733—737).—For the simultaneous estimation of carbonic anhydride and hydrogen sulphide, Fresenius has given a method depending on the retention of hydrogen sulphide by copper sulphate (this Journal, 1871, p. 582); but for the direct estimation of carbonic anhydride under conditions which involve the simultaneous formation of  $\text{SO}_2$  and  $\text{SH}_2$ , as in the examination of crude soda, soda-lyes, &c., no accurate method has hitherto been published. This object may however be attained by the following method, depending on the principle that potassium permanganate, under conditions already described (p. 151 of this volume), converts the sulphides, sulphites, and thiosulphates of the alkali-metals almost entirely into sulphates, so that when a mixture of these salts with carbonates has been thus treated, its subsequent decomposition by an acid gives rise to the evolution of nothing but carbonic anhydride.

The method is applied as follows:—The substance is introduced into a 300 c.c. flask closed by a perforated caoutchouc stopper, through one of the holes of which is inserted a stoppered funnel-tube reaching nearly to the bottom of the flask, and through the other a tube connecting the flask (1) with a Liebig's bulb-apparatus containing an acidulated solution of permanganate; (2) with a  $\text{CaCl}_2$ -tube; (3) with a bulb-apparatus containing caustic potash; (4) with a  $\text{CaCl}_2$ -tube. The apparatus having been made air-tight, a concentrated solution of permanganate is poured in slight excess into the flask, and the carbonate is then decomposed with dilute nitric, sulphuric, or acetic acid (not by hydrochloric acid); the stopcock of the funnel-tube is then closed, and the decomposition of the carbonate is completed by heating the liquid gently at first, and ultimately to the boiling point. The heating is then discontinued; the cock of the funnel-tube is opened; this tube is connected either with a U-tube filled with lumps of solid potash, or with a wash-bottle containing potash-lye; and a slow stream of air is drawn through the apparatus for half to three-quarters of an hour, after which the apparatus may be disconnected. The insertion of the bulb-tube containing the permanganate solution is for the purpose of retaining any portion of  $\text{SO}_2$  or  $\text{SH}_2$  that may have escaped oxidation in the flask.

The accuracy of the method may be judged of by the following examples, in the first and second of which pure sodium carbonate,  $\text{Na}_2\text{CO}_3$ , was mixed with sulphite; in the second with thiosulphate; in the third with sulphide, sulphite, and thiosulphate together; in the fourth with potassium sulphide, sodium sulphite, and sodium

thiosulphate; and in the fifth a mixture of Iceland spar, barium sulphite, and barium thiosulphate was decomposed by dilute nitric acid.

	CO <sub>2</sub> found.	CO <sub>2</sub> calculated.
1.....	41·54 per cent.	} 41·51 per cent.
2.....	41·34     "	
3.....	41·35     "	
4.....	41·33     "	
5.....	43·75     "	44·00     "

In one case in which the absorption-apparatus containing permanganate was not introduced, a mixture of sodium carbonate and sulphite gave 47·01 per cent. CO<sub>2</sub>, whereas the amount according to calculation should have been only 41·51.

This method also gives the means of determining the amount of sulphur contained in the sulphur-compounds mixed with the carbonate. For this purpose, after the carbonic anhydride has been determined as above, the contents of the reaction flask and of the absorption-tube containing permanganate are poured into a beaker, the excess of permanganate and the precipitate of manganite formed in the reaction are decomposed by heating with hydrochloric acid, and after the chlorine has been expelled by boiling, the sulphuric acid is precipitated by barium chloride, &c.

H. W.

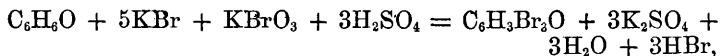
**Estimation of Phosphoric Acid in Manures.** By GASSEND and CAMPREDON (*Ann. Agronomiques*, 9, 266—270).—After having obtained the precipitate of ammonio-magnesian phosphate, there are two ways of dealing with it in common use: it is either calcined and weighed as magnesium pyrophosphate, or it is dissolved in acetic acid and titrated with standard uranium acetate. The authors state that, when applied to commercial fertilisers, the first method invariably gives results which are too high, unless solution of the precipitate in hydrochloric acid and reprecipitation are resorted to, necessitating a further delay of over twelve hours. Titration with uranium acetate they believe to be quite accurate and more expeditious than the gravimetric method, even when only one precipitation is employed. A sample of mixed bone superphosphate and precipitated phosphate gave the following percentages of P<sub>2</sub>O<sub>5</sub>:—

	Uranium method.	Gravimetric method.
P <sub>2</sub> O <sub>5</sub> soluble in water.....	14·08	15·35
„     „     ammonium citrate	14·99	16·18
„     total.....	16·11	17·14

The excess by the gravimetric method was proved to be due to impurities retained by the magnesium precipitate, consisting of iron and alumina (traces), lime, sulphuric acid, and silica. The mean quantity of silica in the three precipitates was 0·008 gram, and the authors find that the ammonio-magnesium phosphate retains silica, even after a day's washing with dilute ammonia.

J. M. H. M.

**Testing of Potassium Bromate.** By G. VULPIUS (*Arch. Pharm.* [3], 21, 186—190, and *Dingl. polyt. J.*, 249, 47).—For the determination of phenol, according to the equation—



the new German Pharmacopeia stipulates the use of normal solutions of potassium bromide and bromate. The latter, according to Vulpius, often contains a large proportion of potassium bromide, which may be estimated in the following manner:—0.1 gram of the bromate is mixed in a tared beaker with 2 grams of potassium iodide, and the mixture dissolved in 5 c.c. of hot water; 10 c.c. of cold water, and 15 grams of a 25 per cent. solution of hydrochloric acid are then added, and the solution is titrated with decinormal sodium thiosulphate. 1 c.c. of this solution corresponds with 2.785 mgrms. of potassium bromate, taking the equivalent for potassium bromate at 167.1. D. B.

**Action of Ammonium Sulphide on Metallic Pyrophosphates.**

By G. BUCHNER (*Arch. Pharm.* [3], 21, 115—120).—The author has investigated the action of ammonium sulphide on the solution obtained by adding excess of sodium pyrophosphate to solutions of the salts of those metals which, in the ordinary course of analysis, are precipitated by ammonium sulphide. If sodium pyrophosphate (5 per cent. solution) is added to solutions of the salts of these metals, a precipitate is obtained which is soluble in excess of the reagent. The addition of ammonium sulphide to this solution precipitates the metals as sulphides in the case of zinc, cobalt, nickel, and iron (ferrous and ferric), but produces no precipitate with manganese (manganous and manganic), uranium, chromium, or aluminium. When these last-mentioned solutions are heated, or allowed to stand for some time, the manganese is precipitated as pyrophosphate of manganese, ammonium, and sodium ( $\text{MnNH}_4\text{NaP}_2\text{O}_7$ ). The solutions containing aluminium and chromium become turbid, if boiled and subsequently cooled; but in the case of uranium the solution remains clear even after boiling. If a solution of an iron salt is precipitated by ammonium sulphide, and a solution of sodium pyrophosphate subsequently added, the ferrous sulphide dissolves when the liquid is boiled, forming a colourless solution, which becomes dark green on cooling, and finally deposits nearly all the iron as sulphide. When a solution of manganese salt is treated in a similar way, the liquid deposits crystals of manganese sodium ammonium pyrophosphate. W. R. D.

**Specific Gravity of Commercial Copper.** By D. WATSON (*Dingl. polyt. J.*, 249, 48).—The author found that copper, when precipitated electrolytically from a solution of the sulphate, has a sp. gr. of 8.955. The sp. gr. of copper is materially affected by different impurities contained in the metal, cuprous oxide having the greatest effect: the following table illustrates this circumstance:—

	Sp. gr.	With $\frac{1}{4}$ p.c. Pb.	With $\frac{1}{2}$ p.c. As.	With $\frac{1}{4}$ p.c. Pb and $\frac{1}{2}$ p.c. As.
Copper free from $\text{Cu}_2\text{O}$ .....	8·955	8·961	8·939	8·945
Copper containing 1 p.c. $\text{Cu}_2\text{O}$ ...	8·925	8·931	8·909	8·915
Copper containing 2·5 p.c. $\text{Cu}_2\text{O}$ ..	8·881	8·887	8·865	8·871

The author is of opinion that the sp. gr., in conjunction with the estimation of lead and arsenic, suffices to approximately determine the amount of cuprous oxide in a sample of commercial copper.

D. B.

**Estimation of Carbon in Cast Iron.** By A. A. BRENNEMAN (*Chem. News*, 48, 168).—In the process recommended, the carbonaceous residue obtained when cast iron is dissolved, is filtered in a small platinum tube, which is subsequently put, with its contents, into the combustion tube and burnt in oxygen. The platinum tube is made of stout foil, and is fitted with a small disc of perforated platinum to support the asbestos for filtering; the air-tight connection, with the necessary glass tube, is made by means of soft india-rubber tubing, one end of which is inserted in the platinum. The ends of the glass tube are conical, so that the connection may be made without injury to the platinum. Combustions should be conducted in porcelain tubes, as these last longer and can be heated more strongly than glass tubes, and the platinum tube should be made to fit well, so that the oxygen may pass mainly through the filter and its contents.

D. A. L.

**Apparatus for Estimating Carbon in Steel.** By A. B. CLEMENCE (*Chem. News*, 48, 206).—The author has introduced an apparatus to avoid the errors attached to the old process of filtering in a glass funnel, &c., and to do away with the expense and inconvenience of the platinum funnel, porcelain tube, combustion furnace method (preceding Abstr.). The apparatus consists of a platinum tube  $11\frac{1}{2}$  inches long, with a diameter of  $\frac{3}{4}$ -inch for 7 inches, the remaining  $4\frac{1}{2}$  inches being  $\frac{3}{16}$  inch diameter. In use, an asbestos plug is placed at the point in the tube where the contraction commences, the carbon is filtered on this, washed well with hot water, any adhering carbon being swept down by moist asbestos, the tube is then dried at  $150$ — $170^\circ$  for an hour. A hard rubber stopper with glass tube passing through is now put into the wide end, through which the current of oxygen enters, a single thickness of filter-paper, 2 inches wide, being wound round the tube by the stopper, and kept wet by a stream of water; the tube, at the part where the filter is placed, is heated with a Bunsen burner for an hour, at the end of which time the potash bulbs can be weighed. The author takes from 3 to 5 grams of borings, which he dissolves in cuprammonium chloride, 36 grams to 120 c.c. water for 3 grams of steel; when the deposited copper is completely dissolved, he proceeds as above described. Good results have been obtained.

D. A. L.



**Volumetric Estimation of Manganese.** By J. B. MACKINTOSH (*Chem. News*, **48**, 176—177).—It has been suggested that the precipitate obtained by treating the boiling nitric acid solution of a manganese salt with potassium chlorate is not pure  $\text{MnO}_2$ , but a mixture of  $10\text{MnO}_2 + \text{MnO}$ . This being of importance in the titration of manganese, the author has studied the subject, and publishes his observations in the present paper.

The experiments are based on the facts that potassium permanganate has an oxidising power equal to five of oxygen for every two of manganese, and that the same quantity of manganese, in the state of dioxide, has an oxidising power equal to 2 atoms of oxygen; so that, if a solution of permanganate is reduced to dioxide, the oxidising power of the dioxide thus formed will be equal to that of two-fifths the quantity of the permanganate solution originally taken. The analyses were conducted in the following manner:—The permanganate was decomposed with hydrochloric acid and concentrated. The hydrochloric acid was removed by boiling with excess of nitric acid, and the manganese precipitated by successive alternate additions of potassium chlorate and nitric acid, until no more yellow fumes were observed. When cool the precipitate was filtered through asbestos, washed with nitric acid and with water, and then treated with a volume of oxalic acid, with a known permanganate equivalent, and a little sulphuric acid. The excess of oxalic acid was determined by permanganate, and the oxidising power of the precipitate found by subtracting the excess from the whole quantity. The results obtained are as follows:—

Permanganate used.	Oxidising power of precipitate in terms of permanganate.	Theoretical for $\text{MnO}_2$ .	Per cent. of theoretical corrected for burette error.	Average true per cent.
45 c.c.	17.80 c.c.	18 c.c.	99.37	—
35	13.93	14	100.07	99.99
25	9.90	10	99.86	—
15	5.96	6	100.67	—

Great importance is attached to the method of precipitating the manganese; for by adding the potassium chlorate at once, and boiling until the action ceases, an error of from 1 to 2 per cent. is almost certain. The author points out that not too much value must be set on the above results, as of course there are many experimental errors involved in the process. It is, however, safe to conclude that the precipitate obtained in this process, when the necessary precautions are taken, is not  $10\text{MnO}_2 + \text{MnO}$  (which would have an oxidising power = 90.91 per cent.) but  $\text{MnO}_2$ . D. A. L.

**Arsenic in Glass.** By W. FRESenius (*Chem. News*, **48**, 147).—In connection with the removal of arsenic from apparatus, &c., used in cases of judicial investigation, the author has observed that the glass of the vessels employed contained arsenic. A sample of Bohemian glass contained 0.20 per cent., of hard glass 0.08, and another sample of hard glass a trace. The author attributes the

browning of glass when heated to arsenic and not to lead. Further experiments show that alkaline solutions take up arsenic from glass; D. A. L. acids do not.

### Microscopic Examination of Water for Organic Impurities.

By J. BRAUTLECHT (*Chem. News*, **48**, 180).—100 c.c. of the water are treated with five drops of a solution containing 1 part of aluminium sulphate, 1 part hydrochloric acid, and 8 parts of water, and one to three drops of ammonia; the precipitate is filtered off and redissolved in 10 to 15 drops of dilute acetic acid; and the clear solution thus obtained is examined under the microscope both before and after the addition of saffranine. By the addition of  $\frac{1}{2}$  per cent. gelatin, permanent preparations on Koch's principle may be obtained.

D. A. L.

### Detection and Estimation of Trinitrophenol (Picric Acid).

By G. CHRISTEL (*Arch. Pharm.* [3], **21**, 190—200).—This paper contains an examination of the principal reactions of trinitrophenol made with a view to its qualitative detection and quantitative estimation. The aqueous solution of picric acid is not precipitated by neutral solutions of lead or copper salts; neither is ammonium picrate, unless the solution is alkaline, when lead acetate gives a reddish-yellow precipitate, and copper sulphate a yellowish-green precipitate in dilute solutions, and a bright green in concentrated solutions. A solution containing half a milligram of picric acid in 5 c.c. of water is not at once precipitated by a solution of cuprammonium sulphate, but on standing for 24 hours a distinct precipitate is obtained, which is insoluble in ammonia, but is decomposed by water. Solution of basic lead acetate is a very delicate test for picric acid, yielding a bright yellow precipitate. A solution containing the tenth of a milligram of picric acid in 5 c.c. of water, gives after 12 hours a distinct precipitate, and a solution containing the twentieth of a milligram in 5 c.c. of water a strong opalescence, which subsequently forms a distinct sediment. When this sediment is decomposed by the addition of 1 drop of sulphuric acid, and the solution is rendered alkaline with ammonium hydrate and evaporated to dryness, a residue is left which, when dissolved in a little water and warmed with a drop of potassium cyanide solution, gives a distinct red colour. The yellow colouring matters of the bark of *Quercus tinctoria* (quercitron), and the root of *Broussonetia tinctoria* also give precipitates with basic and neutral lead acetate, but the precipitates do not give the reaction with potassium cyanide when treated as above described. An aqueous solution of methyl green precipitates solutions of picric acid. The green precipitate dissolves in ammonia, forming a deep yellow solution, which is precipitated by basic lead acetate, and this precipitate gives the reaction with potassium cyanide. This test cannot be applied for the detection of picric acid in beer, for 1 litre of beer which contained 5 mgrms. of picric acid was not precipitated by a solution of methyl green. Solutions of picric acid are precipitated by stannous chloride, and if a small quantity of ammonia is added, the solution becomes red. The same reaction is obtained when a solution, prepared by adding potassium

hydroxide to a solution of stannous chloride until the precipitate at first formed is redissolved, is added to a solution of picric acid. The red colour is due to the formation of dinitroamidophenol (picramic acid): hydrogen and ammonium sulphides give a similar reaction. If a solution of picric acid or a picrate is acted on with zinc and dilute sulphuric acid, a yellowish-red turbid solution is obtained, which, when poured off and mixed with alcohol, develops a green colour, changing through blue to a violet-green. For the detection of picric acid in sweetmeats or other coloured substances containing sugar, the potassium cyanide reaction can be applied directly; or the colouring matter may be extracted with alcohol, the residue from this solution, after dissolving in water, precipitated by lead acetate; and the potassium cyanide reaction obtained after decomposing the precipitate in the manner above described. For the detection of picric acid in wool or cellulose, the hydrochloric acid solution may be reduced by zinc, and the reaction with alcohol obtained. The substance may also be digested with ammonia, and the potassium cyanide reaction tried with this solution. The detection of picric acid in beer cannot be accomplished by means of lead acetate, on account of the other substances in the liquid, which are precipitated by this reagent; neither can the colouring matter be removed by animal charcoal, for this also retains the picric acid. For the detection of picric acid in beer, the author recommends the following method:—200 c.c. of the beer are evaporated to a syrupy consistence on the water-bath, and then digested in a flask with 50 c.c. of alcohol (90 per cent.), the mixture being allowed to stand for 24 hours, when it is filtered, and the residue washed with 31 c.c. more alcohol. The mixed filtrates are evaporated to the consistence of a syrup and acidified with two or three drops of dilute sulphuric acid. The mixture is then extracted with five or six times its volume of ether, the latter removed, the solution again acidulated and extracted with ether. The ethereal solutions are spontaneously evaporated, and the residue dissolved in 5 or 10 c.c. of water, the solution filtered, neutralised with ammonia, and tested by one of the methods above described. For the estimation of picric acid, the author proposes a colorimetric method, based on the potassium cyanide reaction. The ethereal residue is diluted to 10 c.c. with a little ammonia, 5 or 10 drops of a 10 per cent. potassium cyanide solution added, and the liquid, after heating it to 80°, is diluted to 100 c.c. with dilute ammonia. The colour produced is compared with that given by a certain quantity of a standard solution of picric acid, 100 c.c. of which contain 0.1 gram of pure picric acid, the operation being conducted in the same way.

W. R. D.

**Detection of Hydrocyanic Acid in Chemico-Judicial Investigations.** By H. BECKURTS (*Chem. News*, 48, 199).—After pointing out that the presence or absence of hydrocyanic acid or poisonous metallic cyanides in the presence of a harmless cyanide, is not efficiently demonstrated by treatment with tartaric acid and distillation, &c.; the author recommends as efficient, Jacquemin's process, namely, distilling the sample to be tested with concentrated solution of sodium hydrogen carbonate, and testing the distillate for hydrocyanic acid;

or Barfoed's process, in which the mass is acidified with sulphuric or tartaric acid and agitated with ether, which takes up hydrocyanic but not hydroferrocyanic acid.

D. A. L.

**Soap Analysis.** By A. R. LEEDS (*Chem. News*, **48**, 166—168).—The soap, cut in thin shavings, is dried at 100°; the loss is *water*. It is then exhausted with light petroleum, and the extract containing the *free fats* is dried and weighed. The residue is exhausted with 95 per cent. alcohol, and the extract of it containing any *free soda* is titrated with sulphuric acid, using phenolphthaleïn as indicator. The neutralised liquid is largely diluted with water, the alcohol boiled off, and a large excess of normal sulphuric acid added. The whole mass is boiled, cooled and filtered, and the precipitate of *fatty acids and resin* is well washed with hot water, then dried, and weighed. The *resin* is determined by Gladding's method (*Amer. Chem. J.*, **3**, 416), and the amount subtracted from the last total, the difference being the amount of *fatty acids*.

The filtrate from the sulphuric acid is neutralised with normal soda, the *combined soda* calculated, evaporated to dryness, and the *glycerol* extracted with absolute alcohol, dried and weighed; any residue is added to the fatty acid and resin precipitate. The residue from the first alcoholic exhaustion is washed with cold water; the washings are divided into four equal parts; and the *sodium carbonate, chloride, sulphate, and silicate* determined in the separate portions. The residue containing the *starch* and *insoluble inorganic matter* is dried and weighed, the starch being subsequently converted into glucose, and titrated with Fehling's solution.

D. A. L.

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## Technical Chemistry.

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**Employment of Limed Coal in Gas Making.** By J. A. WANKLYN (*Chem. News*, 48, 174—176).—The coal is mixed with  $2\frac{1}{2}$  per cent. of lime previous to being put in the retort. The lime is slaked before mixing. The author claims many advantages for this introduction, viz., increase in the yield of ammonia to the extent of 20—36 per cent.; of liquor to the extent of about 35 per cent.; of tar 6 per cent.; and of gas, which is also improved in quality, being fragrant instead of unpleasant to the smell, and not deteriorated in illuminating power. These advantages are supplemented by a considerable decrease in the quantity of hydrogen sulphide and carbon bisulphide, and in fact the author anticipates the abolition of lime-purifiers if this liming (Cooper's) process is introduced. The coke, too, is much improved by this addition of lime; it is more readily combustible, and does not give off sulphurous anhydride when burnt. In the author's opinion gas works will cease to be the nuisance they now are when the process is introduced.

D. A. L.

**Methods for Coking Coal.** By W. SMITH (*Chem. News*, **48**, 185—187).—In the present paper the author reviews the various methods now employed for the production of coke from coal. The simplest, the *Meiler* or *mound* method, is that in which the coal is burnt in mounds, similar to those employed for the production of wood charcoal; the coke produced is good, and freer from sulphur than oven-coke, but it is not so hard. The *beehive oven* produces a coke almost unsurpassable for metallurgical purposes, but wastes all by-products. The *Appolt oven* and the *Coppée oven* are constructed so as to use the gases and vapours produced during the coking for heating the ovens. The coke is excellent. The *Jameson oven* is a modification of the beehive oven, and is constructed with a floor of perforated quarles instead of the solid floor of the latter; these perforations are connected with a short vertical flue below the floor, and from this a pipe passes at right angles to the hydraulic main, and to exhaust appliances, the exhaustion being carried on as is usual in gas works. The gas produced is not employed in the operation, and can therefore be conveyed to a distance and used for heating purposes. The coke is good. The ammoniacal liquor contains a large quantity of ammonium sulphate, and according to Jameson, the yield of liquor is equal to a production of 5—15 lbs. ammonium sulphate for a ton of coke. The yield of tar or “oils” is from 6—15 gallons per ton of coke; it contains neither benzene, nor naphthalene, nor anthracene, only a small quantity of toluene, but large quantities of xylene mixed with paraffins. The chief bulk of the Jameson tar consists of oils (sp. gr. 0.960, and boiling at 250—350°), which are of little value for burning, and of only secondary value as lubricants. They have no fluorescence. A considerable proportion of the oils distils above 350°, and deposits paraffins, melting at 58°. The oils boiling between 200° and 300° contain a fairly large proportion of phenols, some of which resemble the constituents of wood-tar creasote. They contain a mere trace of phenol, but more cresols, and the largest quantity boils from 250—300°. The 300° fraction is resinous, and perfectly soluble in caustic soda, with a red colour. Some other of these phenols yield reds and blues with alkalis, but of no stability or value. In *Simon-Carvès oven* the coking process is one of destructive distillation, and is similar to that of a gas works. The temperature employed is very great, 2200° or even 3000° being reached. The gas is burnt in the ovens. The ammoniacal liquors are of good strength, 6—7° T. The tar, black and thick (sp. gr. 1.20), is exceedingly rich in naphthalene and anthracene, contains as much benzene, toluene, xylene, and phenol as any London tar, and is moreover free from paraffins. The coke is very good; it has not the silvery glance of the beehive and Jameson oven coke, but is quite as solid, hard, and compact. These properties are obtained by using large charges of coal (4½ tons), piled up in masses of great height (6 feet or so), and considerable thickness (19 inches), but not too thick for the heat of the oven to penetrate sufficiently well. Mellor has introduced a process for separating the benzene from gas, which consists in washing the latter with strong nitric acid in earthenware towers filled with broken glass, and as benzene is soluble in nitrobenzene, the same acid strengthened with sul-

phuric acid is repeatedly passed down the tower. The benzene can be removed from this solution by steam-distilling. Another process with the same object in view is due to G. E. Davis: refrigerated coal-gas is washed with refrigerated heavy coal-tar oils, which remove the benzene. The author is of opinion that the Simon-Carvès method, especially if combined with one of these benzene removing processes, is the coking process of the future. D. A. L.

**Atmospheric Dust.** By A. SCHUSTER (*Bied. Centr.*, 1883, 354).—Sand taken from the neighbourhood of the Great Pyramid, and Nile mud contain a considerable quantity of magnetic particles, some measuring 0.1—0.2 mm. These particles may be derived from exploded meteorites, which by reason of insufficiency of oxygen in the upper atmosphere have not yet been oxidised. E. W. P.

**Existence of Germs in the Air at Great Heights.** By P. GIACOSA (*Gazzetta*, 13, 176).—The author's experiments were made on the summit of Monte Marzo (2756 m. above sea-level), and at the foot of the same mountain (2300 m.), with the following results:—Schizomycetes exist in quantities diminishing as the altitude increases. Throughout the experiment (first three days of August) the air on the top of the mountain contained germs of leaven, and the air at the foot of the mountain was sometimes found to contain cells of the same fungus. Germs of the common moulds are likewise abundant at both altitudes. In no instance were any forms observed which could be referred to animal organisms. H. W.

**Properties of Antiseptics and of the Volatile Products of Decay.** By G. LE BON (*Bied. Centr.*, 1883, 350—352).—The action of antiseptics is weaker the further the decomposition has proceeded. The best antiseptics are as follows, commencing with the strongest:—Potassium permanganate, chloride of lime, ferrous sulphate acidified with acetic acid, phenol, and sodium and potassium glycolates. The action of these compounds as antiseptics is different from their action as microbes; they cannot arrest decay, but may prevent its commencement. As a rule antiseptics have but little action on bacteria; in phenol these organisms live for a long time. At present it is uncertain whether the volatile alkaloids from decomposing animal matter are poisonous, but in a few cases death has occurred after inhaling the volatile products given off by decomposing matter. It is dangerous to exhume a corpse, and the air of churchyards is poisonous. E. W. P.

**The Future of the Chlorine Industry.** By F. HURTER (*Dingl. polyt. J.*, 249, 126—133).—The only hope that the Leblanc process will not be completely wrecked by the ammonia-soda process is that the world requires chlorine as well as soda. Weldon, Solvay, and Mond are doing their best to combine the manufacture of chlorine with the ammonia-soda process. The author attempts to show in what way the ammonia-soda process may endanger the manufacture of chlorine, and how the same may be prevented.

1. *Replacing Chlorine by other Bleaching Agents.*—Perceiving the difficulty of utilising the chlorine from the calcium chloride liquors obtained in the ammonia-soda process, Mond has recently patented a very ingenious method for obtaining calcium peroxide, and for its application as a bleaching and disinfecting agent, but as calcium peroxide is insoluble, it will probably be necessary to convert it into hydrogen peroxide by treatment with a dilute acid, before it can be used for bleaching, &c. The process consists in introducing into a cupola dried blocks of a mixture of barium carbonate, pitch, and sawdust, and heating to about  $1200^{\circ}$ . The barium carbonate is converted into barium oxide, and the carbonaceous products are burnt out. The mass as it descends meets a current of air, which cools the oxide to about  $500^{\circ}$ , when it absorbs oxygen and is changed into barium peroxide. This when cold is decomposed by means of carbonic anhydride and water, under pressure, into barium carbonate and hydrogen peroxide. The former is used afresh, whilst calcium peroxide is prepared from the hydrogen peroxide by adding milk of lime to it. Calcium peroxide is a hydrate of the formula  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ , containing 7.4 per cent. of available oxygen, equivalent to 32.8 per cent. of available chlorine. According to Lunge, the manufacture of barium hydroxide is carried out on a large scale in France, and consequently the production of the peroxide should present no difficulty.

The peroxides are all very powerful oxidisers. According to Thomsen, the amount of heat produced by oxidation with hydrogen peroxide is 23,064 units larger per molecule than by the direct oxidation with free oxygen. In spite of its energetic oxidising action, hydrogen peroxide is so slow a bleaching agent that it appears as though it is not available oxygen but chlorine that is required for the bleaching of vegetable fibres. Gerhardt attributes the bleaching action of chlorine to the facility with which it is substituted in organic substances in the place of hydrogen. The author has found that by igniting bleached cotton with soda the presence of chlorides can be detected in the melt, whilst unbleached cotton when similarly treated does not exhibit this reaction. Hydrogen peroxide is the only compound which could be prepared cheaply enough to compete with bleaching powder, but on account of its slow action competition will be impossible. Other bleaching agents have from time to time been recommended, all of which are in reality oxidising agents. If, therefore, available chlorine and not oxygen effects the bleaching of vegetable tissues, it is highly improbable that these substances will ever supersede chloride of lime.

2. *Production of Hydrochloric Acid.*—It has not yet been possible to prepare chlorine directly from sodium chloride. In the Leblanc process the sodium in common salt is replaced by hydrogen derived from sulphuric acid, which costs nearly 2000 marks per ton, whilst in the ammonia-soda process it is calcium, which costs only about 15 marks per ton. Besides calcium and hydrogen, there are no elements suitable for the purpose which could be obtained at a smaller cost.

Solvay and Weldon have been endeavouring to utilise the calcium chloride liquors for the preparation of chlorine. Their process con-



sists in replacing the calcium in calcium chloride by hydrogen. The calcium chloride is mixed with clay, formed into lumps, and subjected to the action of superheated steam at a high temperature. A very dilute hydrochloric acid is produced, from which the excess of steam is removed by the addition of concentrated calcium chloride liquors before the hydrochloric acid is condensed. The process is not only very costly, but requires a very large plant. It is therefore not likely to endanger the Leblanc process, which promises to remain the chief source of chlorine.

Vorster and Grüneberg recommended some years ago to heat sodium chloride and clay, and obtain sodium silicate and hydrochloric acid. Their process, however, was abandoned, as the reaction was found to require an extremely high temperature, and the cost for repairs was too excessive.

*Other Chlorine Processes.*—By decomposing sodium chloride with sulphuric acid, the resulting gaseous or liquid hydrochloric acid can be used for the preparation of chlorine, according as the Deacon or Weldon process is employed. With Hargreaves' process liquid hydrochloric acid only can be used, as the gas contains too much nitrogen and too little oxygen. The conversion of hydrochloric acid into chlorine necessitates the presence of another element with which to combine the hydrogen, the only element which has a greater affinity for hydrogen than chlorine being oxygen. The affinities between hydrogen and chlorine and hydrogen and oxygen approach each other so closely that the mere change from the liquid state to that of a gas alters the proportions. In consequence of these variations a direct decomposition of liquid hydrochloric acid by oxygen is impossible, whilst in the gaseous form hydrochloric acid can be decomposed directly by oxygen. To prepare chlorine from liquid hydrochloric acid a certain amount of chemical energy must be supplied in addition to oxygen, *i.e.*, nascent oxygen, which is liberated from an oxide with evolution of heat, is required. Since the oxide must contain more oxygen than is equivalent to the chlorine, which afterwards forms chloride, a peroxide is required. There is no better material than manganese for the purpose. Although barium and lead form two oxides and only one chloride, the transformation of the chloride into peroxide in the case of barium will always be difficult on account of the large differences in the heat of formation of the two compounds, whilst in the case of lead, its price and high equivalent weight render it useless. Weldon's process can be superseded only by a peroxide which is cheaper than the expense of recovering the manganese dioxide, or which itself can be regenerated at a less cost. The disadvantage in connection with the Weldon process is that it only yields theoretically one-third of the hydrochloric acid as chlorine. This difficulty is said to be removed by Weldon's new process (No. 2). Magnesium manganite obtained by process No. 1 is decomposed with hydrochloric acid in the chlorine stills. One-fourth the chlorine contained in the hydrochloric acid is generated, and a solution of manganese and magnesium chlorides formed. The latter is evaporated to a syrupy consistency, mixed with a certain amount of solid manganite, formed into balls, intro-

duced into an apparatus similar to the Hargreaves, and exposed to a current of heated air, when 90 per cent. of the chlorine contained in the mixture is liberated, magnesium manganite being formed.

The author is of opinion that where still-work has to be done, the chloride of lime cannot be obtained at a lower cost, as the only saving in Weldon's new process is the lime required for oxidation, about 500 kilos. of bleaching powder; the labour in this process, however, forms a much greater item, so that bleaching powder made by the new process will cost fully as much, if not more than that obtained by the old process.

By comparing the Deacon process with Weldon's No. 2, we find that it is the only process in use in which gaseous hydrochloric acid can be decomposed into chlorine by a simple reaction,  $2\text{HCl} + \text{O} = \text{H}_2\text{O} + \text{Cl}_2$ , accompanied by evolution of heat. The decomposition is accelerated by catalytes. On account of its capability of being dissociated at a high temperature, cupric chloride is the cheapest and most efficient catalyte; moreover, copper is the only metal which forms two oxides and two chlorides, in all of which the combination is of a very loose character. It appears, therefore, highly probable that the Deacon process will continue to be the only one available for the conversion of gaseous hydrochloric acid into chlorine.

The author concludes this paper with the following remarks:—No other chloride is better adapted for the manufacture of chlorine than hydrogen chloride. If the latter is to be decomposed in the liquid state, the decomposition can be effected only by means of manganese dioxide, as there is no other peroxide so readily regenerated from the chloride. If hydrogen chloride is to be decomposed in the gaseous state catalytes are required, and should it be possible to obtain a cheaper catalyte than copper the apparatus now in existence would be equally applicable. Neither the Weldon process nor the Deacon process is perfect; both are capable of improvement, especially the Weldon process, inasmuch as the quantity of chlorine which it yields is considerably less than that which should be obtained from the hydrochloric acid consumed.

D. B.

### **Schaffner and Helbig's Process for the Recovery of Sulphur.**

By A. M. CHANCE (*Dingl. polyt. J.*, **249**, 33—35).—Chance (*Jour. Soc. Chem. Ind.*, **2**, 202) gives an interesting account of his results and experiences in working with the Schaffner and Helbig sulphur recovery process. The residue is worked up in the decomposers in the following manner:—The solution of magnesium chloride—whose temperature must not exceed  $60^\circ$ , otherwise sulphuretted hydrogen will be evolved—is introduced into the decomposer, and the residue is thrown in, after which the mixture is heated by means of wet steam, in order to expel the air above the charge, and prevent its admission into the decomposer; thus the formation of an explosive mixture is rendered impossible. The heating by means of dry steam is then proceeded with, the mixture being well agitated all the time. The best results are obtained with jacketted decomposers, although

cast-iron steam coils are attacked less readily than wrought-iron jackets. For carbonating the liquors containing magnesium hydroxide and calcium chloride, vertical vessels without agitators are the most useful. The deeper the column of liquid and the greater the percentage of carbonic anhydride, the quicker and better are the results obtained. The average strength of the carbonic acid gases was 26 per cent. To work off 8 tons of residue from five to six hours are required. The lime mud is sifted, filter-pressed, and washed. The first washings are concentrated in steam boilers, together with the stronger liquors, whilst the last washings are thrown away. No mention is made of the action of the magnesium chloride liquors on the plates of the steam boilers. The sulphuretted hydrogen gas is collected in gas-holders, the inlet and outlet being connected with a water-seal to prevent explosions. The burning of the sulphuretted hydrogen gas for the manufacture of sulphuric acid has been a great success, but a satisfactory process of recovering sulphur direct from the gas has not yet been introduced. The loss of magnesium chloride corresponds with 4 to 4·5 tons per 100 tons of sulphate, or 20 tons per 100 tons sulphur, more than one-half the loss being attributable to mechanical defects, which should be gradually reduced.

In discussing the value of the lime mud and its adaptability for the manufacture of soda, Chance shows that, as the mud leaves the presses it contains about 50 per cent. of moisture, which must be removed, an operation which in itself is a great disadvantage; moreover, the resulting crude soda contains large quantities of chlorides as well as calcium carbonate. Referring to the probable cost of working the process, a detailed estimate is given, from which it is concluded that it would no longer pay should the price of pyrites be reduced by one-half, especially if it were found that the resulting lime mud was of no value for black ash making. The future of this process depends on a good method of extracting pure sulphur from the generated sulphuretted hydrogen.

Weldon mentions that England and America alone consume 150,000 tons of Silician sulphur per annum, or 50 per cent. more than the total quantity capable of being yielded by the whole English soda industry. Schaffner's sulphur, which is absolutely pure, should easily displace Sicilian sulphur. As to the market price of sulphur, Muspratt and Mactear show that, although recovered sulphur has been offered at considerably less than Sicilian sulphur, great difficulty has been experienced in selling it.

Hurter gives analyses of soda waste and soda liquors obtained from crude soda made exclusively from recovered lime mud by Chance. The waste obtained from four samples of black ash contained in the dry state—

	Soluble soda.	Total soda.	Calcium sulphide.
I.....	0·550	1·77	30·00
II.....	0·440	0·97	33·40
III.....	0·360	1·52	29·1
IV.....	0·175	0·73	23·4

Ordinarily the waste contains 40 per cent. calcium sulphide. 1 litre of the vat liquors obtained from the crude soda contained—

Na <sub>2</sub> O.	NaHO.	Na <sub>2</sub> S.	Na <sub>2</sub> SO <sub>4</sub> .	NaCl.	Na <sub>4</sub> Fe(CN) <sub>6</sub> .
165·2	44·27	5·08	6·77	42·57	0·01 gram.

D. B.

**Manufacture of Sulphuric Acid in America.** (*Dingl. polyt. J.*, **249**, 48.)—Until quite lately sulphuric acid has been manufactured in America almost exclusively from sulphur. On account of the rapid rise in the price of sulphur, the manufacture of pyrites acid has recently been commenced by various manufacturers, but by far the largest proportion of acid is still made from sulphur. The price of American sulphur acid compared with English pyrites acid, is said to be so high that English superphosphate, prepared from American phosphate, can be sold in America at prices against which the American manure manufacturers have a difficulty to compete. The sulphur for 10 tons (= 9071·8 kilos.) sulphuric acid 66° costs 83 dollars; the cost of Spanish pyrites, however, amounts to only 49 dollars.

Besides Rio Tinto pyrites, a variety of native iron sulphide of great purity has recently been brought into the American market. It is obtained from the Davis mine in Massachusetts, and contains 47 per cent. of available sulphur. Zinc, lead, and lime are present only in minute traces, whilst arsenic is quite absent. The following is the composition compared with the Spanish ore :—

	S.	Fe.	Cu.			
Spanish pyrites.....	47·87	40·93	3·82			
Pyrites from the Davis mine ..	50·30	42·83	3·07			
	Pb.	Zn.	CaO and MgO.	As.	SiO <sub>2</sub> .	
Spanish pyrites.....	0·62	0·10	0·19	0·26	5·42	
Pyrites from the Davis mine	0·61				3·19	

D. B.

**Manufacture of Aluminium.** (*Dingl. polyt. J.*, **249**, 86—88.)—It is stated that Salindars is the only place in the world where aluminium is manufactured, about 2400 kilos. of metal being produced annually. The sodium used in the manufacture is obtained by igniting sodium carbonate with carbon in presence of a small quantity of lime, which is said to facilitate the distillation. The double chloride of aluminium and sodium is prepared by strongly heating a mixture of alumina, carbon, and sodium chloride in a current of chlorine. The resulting double chloride is then fused with the sodium in small reverberatory furnaces, cryolite being added as flux.

Much has recently been said in the newspapers with respect to an invention by which it is supposed that Webster of the Aluminium Crown Metal Works, Hollywood, has greatly cheapened aluminium. The preparation of 1 ton of aluminium is said to cost only 2,000

marks. The method consists in strongly heating bauxite with sodium carbonate, decomposing the sodium aluminate with carbonic anhydride, heating the deposited alumina with carbon in a current of chlorine, and fusing the resulting double chloride of aluminium and sodium with sodium and cryolite. This process is neither new nor is it possible to produce aluminium at a lower cost than at Salindars. Webster has also patented a method for preparing alumina for the manufacture of aluminium, which relates to the obtainment of anhydrous alumina from potash alum. The method is impracticable and costly.

Morris obtains aluminium by treating a mixture of alumina and carbon with carbonic anhydride. A solution of aluminium chloride is mixed with pulverised charcoal or lampblack, evaporated to a thick paste, cooled, and made into balls, which after drying are placed in iron tubes and heated. The last traces of chlorine are removed by passing steam through the tubes. The heat is then increased to dull redness and carbonic anhydride introduced. The carbon reduces the carbonic anhydride to oxide, and this is said to reduce the alumina to aluminium.

D. B.

**Electroplating Zinc with Nickel.** By MEIDINGER (*Dingl. polyt. J.*, 249, 90).—Meidinger states that in electroplating with nickel, copper, brass, and iron can be well coated, whilst zinc is coated with difficulty. It is therefore recommended to slightly amalgamate the zinc before it is electroplated with nickel by placing it in a solution of mercuric chloride or nitrate acidified with sulphuric or hydrochloric acid. The nickel then deposits well, adheres firmly, and takes a good polish. It is thought that the zinc plates brought into commerce are treated in this manner, as they are more brittle than pure zinc should be. It is therefore necessary not to let the amalgamation go too far. It has been difficult to electroplate German silver with nickel, and the author is of opinion that in this case also amalgamation would give good results.

D. B.

**Asphalt or Bitumen of Judea.** By B. DELACHANAL (*Compt. rend.*, 97, 491—494).—A specimen of bitumen of Judea, obtained from Palestine through M. de Lesseps, was in the form of large, somewhat friable lumps, very deep brown in colour, but not black, and breaking with a conchoidal fracture. When heated, it gave off hydrogen sulphide, and was found to contain 3.02 per cent. of sulphur. A commercial sample of bitumen of Judea contained 3.14 per cent. of sulphur. The bitumen does not leave more than 0.273 per cent. of ash, hence the greater part of the sulphur does not exist in the form of metallic sulphides. When bitumen of Judea is heated, it softens, melts, and at a sufficiently high temperature gives off hydrogen sulphide and gaseous hydrocarbons, together with a dark-coloured oil, whilst a bulky carbonaceous residue is left in the retort. This oil can be separated into several fractions which closely resemble the products obtained by the distillation of crude petroleum. The oils are partly soluble in fuming nitric acid, leaving a residue of paraffin which solidifies at 15°.

C. H. B.

**Manufacture of Cellulose.** (*Dingl. polyt. J.*, **249**, 23—29 and 124—126.)—The use of sulphurous anhydride in the manufacture of cellulose is becoming of more importance every day. In 1876 Mitscherlich recommended treating finely-divided wood under pressure with a solution of calcium bisulphite obtained by placing calcium carbonate in a tower and introducing water into the top and sulphurous anhydride into the bottom. Paper made from the resulting cellulose was found to be exceedingly tough, and has been sold as a second quality parchment-paper, although it does not possess the qualities which characterise this paper. The details of Mitscherlich's process have since been kept secret. Francke works with solutions of calcium, magnesium, or sodium sulphite of 4° to 5° B., at a pressure of 4 to 5 atmospheres, the operation being completed in 12 to 15 hours. He uses rotary horizontal cylindrical boilers lined with lead, the lining being independent of the outer casing, thus forming a separate boiler. The essential theoretical difference between the lime and the magnesia process is that the resulting calcium sulphate, being almost insoluble, remains in the lignose, whilst the magnesium sulphate is removed during the washing operation. At present it is uncertain whether other differences exist between the two processes.

The cost of pulp by Eckmann's method, depending on the use of magnesium sulphite, is 26 marks per 100 kilos., the selling price being about 40 marks. During last summer this method was tested by a number of French paper manufacturers with the following results:—The quantity of wood employed was 4395 kilos. in the form of fir planks. The loss by removal of knots in chopping, grinding, &c., amounted to 825 kilos. The remaining 3570 kilos. yielded 1437 kilos. dry cellulose corresponding with 32.68 per cent. of the original wood. The latter contained 21 per cent. of moisture, so that the yield on the dry substance is equal to 40 per cent. This is considerably less than the yield obtained by the Francke-Mitscherlich process; the quality of the pulp, however, is far superior. According to recent trials made by Eckmann, it is shown that it is possible to obtain at will either isolated cells or fibrous bundles by using either hydrogen magnesium sulphite, or magnesium sulphite. In the former case, the colouring and glutinous substances are completely dissolved, whilst in the latter case a portion of the gluten remains in the fibres.

Archbold macerates the woody tissue with dilute milk of lime, saturates with sulphurous anhydride at a pressure of 4 to 5 atmospheres, and washes the mass with water.

Tilghman's method consists in boiling in closed vessels wood, esparto or flax, with sulphurous anhydride or calcium bisulphite, or both.

Pictet recommends the use of liquid sulphurous anhydride. Finely-divided wood is first immersed in water, and for every litre 120 grams of liquid sulphurous anhydride is added. At a temperature of 85° a pressure of 7 atmospheres is produced, so that the incrustating substances of the wood are strongly attacked. The pulp has the grey colour of the original wood, but may be easily bleached.

In discussing the sulphite treatment, Bourdilliat contradicts the statement that sulphuric acid is formed when wood is boiled with sulphites; moreover, he believes that the sulphurous anhydride dis-

solves the incrustating substances of the wood, bleaches the colouring matters, and deposits finely-divided sulphur in the fibres, whilst the resins, which are attacked by sulphurous anhydride, form soaps with the base of the bisulphite. These, together with the sulphur, remain in the fibre and add considerably to its weight; the loss during the washing operations is therefore not of fibre but of the mass-compound of sulphur, resin, and lime.

Cross is under the impression that the action of the magnesium sulphite is to prevent the oxidation of wood and lignified cellulose when heated with water under pressure. For comparing the success of the different sulphite processes, the test for lignose with aniline sulphate is said to give unsatisfactory results: it is preferable to treat the cellulose first with chlorine and then with sodium sulphite; if lignose is present, a magenta colour is produced. D. B.

**Alcohol from Melon-juice.** By LEVAT (*Compt. rend.*, **97**, 615—616).—Melon-juice does not undergo fermentation directly, but on boiling it with very dilute sulphuric acid, the sugar in the juice is inverted, and fermentation then takes place readily, 5 litres of alcohol being obtained from 30 kilos. of melons. C. H. B.

**Clouding and Fining of Wines.** By J. NESSLER (*Bied. Centr.*, 1883, 342—344).—Seven varieties of Greek wines, when exposed to low temperatures, become cloudy, but a young wine clouded as the temperature rose; the substance rendered insoluble by the lowering of the temperature redissolved as the temperature rose, but when some wine had been withdrawn from the cask, while it was cloudy, the wine refused to clear. Fining with albumin, &c., prevents cloudiness, and the browning and thickening which so frequently occur are due to decomposed husks introduced during manufacture. To fine wines which have refused to clear by means of albumin, "Spanish earth" (100—200 grams per hectolitre) is recommended; this is also the best material to use in the preparation of sparkling wines.

E. W. P.

**Plastered Wine.** By M. NENCKI (*Bied. Centr.*, 1883, 345—347).—This paper is an answer to questions laid before the author by the municipal authorities of Berne. Plastered wines are not of necessity prejudicial to health, although in a few cases they may be so, and then only when a strongly "plastered" wine has been regularly used. Probably Marsala, &c., which is more strongly "plastered," may be harmful, but the author has no proof as to whether it is or is not so. Natural wines may contain as much as 0.503 gram  $K_2SO_4$  per litre. Plastering should introduce into the wine only a quantity of sulphates equivalent to 2 grams  $K_2SO_4$ , and no more. Free sulphuric acid has occasionally been detected in wine; this arises from the formation of ethyl sulphate, which has been mistaken for the other acid.

E. W. P.

**Barley and Malt.** (*Dingl. polyt. J.*, **249**, 133—139).—Bungener and Fries have found that boiling water containing 1 per cent. salicylic acid, readily dissolves starch, forming a thick syrupy mass, which, on cooling, deposits tabular crystals of starch. On boiling

4 to 5 grams of finely ground barley with 150 c.c. water and 1·5 gram salicylic acid for three-quarters of an hour, all the starch is dissolved. The hot opalescent colourless liquid is filtered, and the residue washed with hot water until the filtrate ceases to react with iodine. Hydrochloric acid is then added to the starch in the filtrate, and the resulting glucose determined by means of copper solution. The results are 1 to 2 per cent. higher than those obtained when the starch is dissolved in water at 135°. In the latter case, a dark-coloured solution is formed, probably due to decomposition.

According to Aubrey, five samples of Alsatian Chevalier barley (1882 crop) contained the following ingredients, calculated on the dry substance:—

	I.	II.	III.	IV.	V.
Starch .....	62·73	58·20	60·39	65·49	66·34
Nitrogen .....	1·9008	1·9456	1·6208	1·6400	1·7456
Proteids corresponding with nitrogen ....	11·88	19·16	10·13	10·25	10·91
Phosphoric acid.	1·053	1·082	1·064	1·030	1·062

Similar samples, from the year 1880, made into malt and dried at 81°, gave the following results:—

The barley contained			Germinating power.	Yield of extract from dry substance per cent.	Maltose in extract per cent.	Maltose: non-maltose = 1	Saccharification in minutes.
Starch.	Nitrogen.	Phosphoric acid.					
62·57	1·659	1·015	99	81·62	63·96	0·56	30
65·35	1·443	0·910	99	84·36	62·32	0·60	45
65·14	1·646	1·115	98	84·09	65·25	0·53	30
61·20	1·646	1·023	97	83·26	63·02	0·58	30
64·20	1·625	0·965	100	80·67	64·17	0·55	30
65·78	1·819	1·098	100	79·70	64·49	0·55	30

Schwarz has investigated different kinds of American barley. He shows that the weight of the grain is no criterion as to the amount of solid matter, starch, proteids (nitrogen  $\times$  6·25), and ash contained in the barley. The subjoined table illustrates the results of his investigation:—



Quality.	Weight of grain.	Per-centage of water.	The dry substance contains			
			Starch per cent.	Proteïds per cent.	Ash per cent.	Phosphoric acid per cent.
Minnesota barley.....	30·9	14·13	67·31	13·58	2·77	1·050
Scotch, quality II.....	35·4	14·35	63·77	13·34	2·82	0·985
Scotch, quality I.....	34·5	11·90	64·85	11·93	2·86	1·031
Choice Scotch.....	31·2	14·33	65·20	11·67	3·28	0·934
Wisconsin barley.....	32·6	16·14	65·47	10·80	2·83	0·997
Scotch Wisconsin barley	35·2	14·34	66·12	9·25	2·74	0·929
Canada, quality II.....	29·0	15·31	65·33	10·27	3·16	0·969
Canada, quality I.....	32·8	16·96	68·53	12·73	3·74	0·996
West Canada.....	30·7	13·29	67·54	11·01	3·02	0·954
Chevalier California....	43·7	13·31	68·33	10·42	2·86	0·980
State barley.....	35·0	11·24	66·35	11·45	2·72	0·935
Canada barley.....	28·6	10·46	66·48	10·47	2·92	0·856

With regard to the changes in weight and volume which barley and malt undergo, Chodounsky found that kiln-dried malt, immediately after being dried, shows a diminution in volume, whilst malt, when kept, increases both in weight and volume. 100 hectolitres of barley yield 97 to 99 hectolitres of kiln-dried malt, and 99 to 101 hectolitres of stored malt.

Lintner states that the defects in the present malting processes are due mainly to the want of uniformity of temperature in the germinating heaps, and the difference in the amount of moisture which exists in the various layers. The gradual discharge of carbonic anhydride, and the defective admission of oxygen, has a marked effect on the malt. These imperfections are said to be removed by the pneumatic malting process, in which the barley, after germination, is thrown on a plate having fine perforations; the air underneath the plate is then exhausted. Thus the heat is withdrawn and the carbonic anhydride removed in a regular stream, so that the germinating grain is situated in a bath of pure air, having always the same temperature and containing the same amount of moisture. To effect this the air is previously purified and heated to the necessary temperature.

D. B.

**The System on which Rice may be Used in Brewing.** By A. MARKL (*Bied. Centr.*, 1883, 348).—The analyses of rice published by Braconnot show that it is better adapted for brewing than barley, but owing to its higher sp. gr., precautions must be taken to prevent its settling to the bottom of the mash-tub; to obtain the best results, the rice must be previously boiled and steamed before mashing; the wort may be strongly hopped, and then kept cool to ensure normal fermentation.

E. W. P.

**Fermentation of Bread.** By G. CHICANDARD (*Compt. rend.*, 97, 616—617).—A reply to Marcato, Mousette, and Bouteux.

**Alteration of Flour by Age.** By BALLAND (*Compt. rend.*, 97, 346—347).—The proportion of water is slightly variable, and alters with the hygrometric condition of the atmosphere. Fatty matters experience no sensible alteration in weight, but become rancid. The saccharine substances decrease in amount, but the diminution bears no relation to the degree of acidity. The degree of acidity depends on the nature of the grain, flour from soft grain becoming acid more rapidly than flour from hard grain. This acidity is apparently connected directly with the alteration of the albuminoids, which at first exist in the form of insoluble gluten, but gradually decompose without loss of weight. The amylaceous constituents would seem to remain unchanged. Flour which has not been finely sifted keeps badly, and is always more acid; it contains a higher proportion of woody, fatty, and saccharine substances, and more gluten. Flour kept in bags alters more rapidly than flour preserved in closed vessels. For the same degree of sifting, flour obtained by millstones keeps as well as that obtained by cylinders; the acidity is independent of the grinding. The farinaceous portion of the grain in contact with the external envelope is more acid than the internal portion; it contains the same amount of gluten, but alters more rapidly. C. H. B.

**Notes on Milk and Butter.** By M. SCHMÖGER and others (*Bied. Centr.*, 1883, 418—419).—Experiments were made to discover whether it is better to cool milk before skimming or not. The instrument used was a tubular cooler, similar to that of Rossler, but with oval tubes instead of circular. It worked well, bringing the milk in a short time to within 2° of the temperature of the water employed. The cooled milk was compared with some from the same milking not artificially cooled; the results were decidedly in favour of the former. Experiments in butter-making were made with the Holstein, Lefeldt, and a rocking churn of American invention, using sweet and sour cream.

	Fat left in buttermilk.	
	Sweet cream.	Sour cream.
Holstein system . . . . .	0·71 per cent.	0·85 per cent.
Lefeldt „ . . . . .	1·51 „	0·84 „
Rocking churn. . . . .	1·20 „	0·50 „

Average duration of process was less by the Holstein process than by the two others. J. F.

**Artificial Butter Colourings.** By E. SCHMITT (*Ann. Agronomiques*, 9, 255—257).—Amongst the substances employed for this purpose, the author enumerates marigold and carthamus flowers, saffron, carrot juice, and turmeric; more recently coal-tar colours have been introduced, such as coralline-yellow and Victoria-yellow, and also lead chromate. The two most widely sold colourings are Krick's "Orantia" and Trannoy's "Carottine"; the author shows that annatto is the basis of both. "Orantia" can be exactly imitated by digesting 50 grams annatto with 100 grams crystallised sodium carbonate, dis-

solved in a litre of water, and evaporating down to half a litre. "Carottine" is a much better preparation, and may be imitated by digesting 125 grams annatto in half a litre of oil; a mixture of equal parts of annatto and turmeric root will give a lighter yellow. It is used in the proportion of a teaspoonful to 25 litres of cream, and the colour diffuses very rapidly and uniformly throughout the butter.

J. M. H. M.

**New Dyestuffs.** (*Dingl. polyt. J.*, 248, 340—343.)—Whereas the monosulphonic acids of phenylamidoazobenzene produce reddish-yellow to orange dyes, the corresponding tri- and tetra-sulphonic acids yield pure yellow shades. For the preparation of the polysulphonic acids of phenylamidoazobenzene,  $\text{NHPh.C}_6\text{H}_4.\text{N}_2.\text{C}_6\text{H}_5$ , 20 kilos. of the latter are treated in the cold with 100 kilos. fuming sulphuric acid containing 20 per cent. anhydride. The mixture is warmed to 60—70°, and the temperature reduced after three or four hours. The mass is then thrown into water, treated with milk of lime, and the calcium compound with the sulphonic acids converted into sodium salts. This polysulphonic acid is obtained also by heating to 70—80° 20 kilos. of the monosulphonic acid with 80 kilos. fuming sulphuric acid, and completing the process as before. These dyes are brought into commerce as potassium or sodium salts in the dry state.

For the production of artificial indigo from the orthamido-derivatives of acetophenone and phenylacetylene, the Badische Anilin und Soda Fabrik treats a concentrated solution of acetylorthamidacetophenone, or of acetylorthamidophenylacetylene in carbon bisulphide in the cold with an equal weight of dry bromine. A crystalline bromine compound is formed, which is dissolved in 10—20 times its weight of concentrated sulphuric acid. Dilution of this with water causes the precipitation of colourless flakes; these dissolve in warm soda solution to a clear deep yellow liquid, from which indigo separates out on contact with the air.

According to the Farbwerke, late Meister, Lucius, and Brüning, tolylaldehyde from metaxylene is converted by nitration into methylorthonitrobenzaldehyde. This on treatment with twice its weight of acetone, and 25 times its weight of a 2 per cent. solution of soda, is readily transformed into methyl-indigo, a substance closely resembling natural indigo, but from which it may be distinguished by its ready solubility in water. From the same source, processes for the preparation of azo-dyes from the trisulphonic acids of  $\beta$ -naphthol are given. The trisulphonic acid is obtained by treating  $\beta$ -naphthol with fuming sulphuric acid containing 20 per cent. anhydride at 140—160°, until the mass gives a pure green fluorescent solution with ammonia. Combined with various diazo-compounds this acid yields yellow, orange-red, and bluish-red dyes, of which the three following are specially adapted for dyeing cotton:—(1.) A red dye, obtained by the action of the diazo-compound of  $\alpha$ -naphthylaminesulphonic acid on sodium  $\beta$ -naphtholtrisulphonate in presence of ammonia. (2.) A bluish-red dye, resulting from the action of the diazo-compound of amidoazobenzene on sodium  $\beta$ -naphtholtrisulphonate in presence of ammonia. (3.) A bluish-red colouring matter, obtained from the diazo-compound of amidoazobenzenesulphonic acid. In the above

three cases the dye is thrown down as a bulky precipitate on mixing a solution of sodium  $\beta$ -naphtholtrisulphonate with that of any of the diazo-compounds. The precipitate is purified by dissolving it in water and reprecipitating with salt. D. B.

**New Coal-tar Dyes.** (*Dingl. polyt. J.*, **248**, 252—256.)—According to C. Reichl, a new phenyl colouring matter is obtained by the cohobation in molecular proportions of an alkaline xanthate and resorcinol dissolved in a small quantity of water or alcohol, so long as carbon bisulphide is returned. Water is added to the dark yellow liquid obtained, which is then filtered, and the colouring matter precipitated with hydrochloric acid from its previous combination with the alkali. It may be obtained by recrystallisation from hot water in slender yellow needles, insoluble in cold, but readily soluble in hot water; alcohol, acetic acid, and alkalis dissolve it with ease. Wool and silk are dyed a brilliant yellow in a weak acid solution. Orcinol, quinol, pyrogallol, naphthol, and quinone similarly treated also yield yellow dyes.

For the preparation of a monosulphonic acid of  $\beta$ -naphthylamine and  $\beta$ -naphthol, the Baden Anilin und Soda Fabrik allow sulphuric acid (96 to 97 per cent.) to act on  $\beta$ -naphthylamine at a temperature of  $100^{\circ}$  to  $105^{\circ}$ , the sparingly soluble modification of the monosulphonic acid being exclusively formed. By converting this into the diazo-compound and decomposing the latter with water,  $\beta$ -naphtholmonosulphonic acid is obtained, the acid sodium salt of which is sparingly soluble in hot alcohol. By evaporating the aqueous solution of the free acid, it is split up into  $\beta$ -naphthol and sulphuric acid. When the alkaline solution of the acid is brought in contact with the diazomonosulphonic acid of azobenzene, orange-coloured flakes are thrown down. This azo-colouring matter dyes ponceau-red shades.

A process for preparing red and brown azo-dyes from anthrol, anthrolsulphonic acids, and dioxyanthracene has been patented by the Actien. Ges. f. Anil. Fab. Berlin. The claims are the pairing of anthrol, anthrolsulphonic acid, anthroldihydride and its sulphonic acid, as well as  $\alpha$ - and  $\beta$ -oxyanthrol with diazobenzene and its homologues, diazonaphthalene, diazoanisole, the sulphonic acids of these diazo-bodies, with diazoanthraminesulphonic acid, diazoamidoazobenzene and its homologues, and mono- and di-sulphonic acids of these diazo-compounds. The products containing the sulphuryl-group are soluble in water, the remainder dissolve in alcohol. D. B.

**Composition of Turkey-red Oil.** By L. LIECHTI and W. SUIDA (*Ber.*, **16**, 2453—2458).—Glycerol trioleate and tricinoleate were treated with sulphuric acid, and the products separated in a similar manner to that employed in the manufacture of Turkey-red oil. The products of the reaction in each case consist essentially of two substances, of which the one is more soluble in ether, the other in water. The compound soluble in water derived from glycerol trioleate is *glyceryl sulphate hydroxyoleate*,  $C_{42}H_{78}O_{12}S = SO_4[C_3H_5(OH).C_{18}H_{33}O_2]_2$ , an oily substance of acid nature, very soluble in water and alcohol, more sparingly in ether, carbon bisulphide, and benzene. When

heated with water, it yields glycerol, hydroxyoleic acid, and sulphuric acid. It unites with bromine in the cold. When mixed in aqueous solution with metallic acetates, it yields salts, of which the following have been analysed:—Copper salt,  $C_{42}H_{74}O_{12}SCu_2$ ; barium salt,  $C_{42}H_{76}O_{12}SBa$ ; silver salt,  $C_{42}H_{76}O_{12}SAg_2$ ; aluminium salt,  $(C_{42}H_{74}O_{12}S)_3Al_4$ ; zinc salt,  $C_{42}H_{74}O_{12}SZn_2$ .

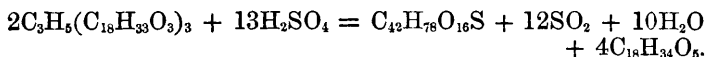
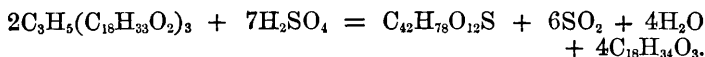
*Glyceryl sulphate trihydroxyoleate,*



the corresponding derivative from glyceryl tricinoleate, closely resembles the preceding compound in all its properties. The following salts have been analysed:—Copper salt,  $C_{42}H_{76}O_{16}SCu$ ; barium salt,  $(C_{42}H_{77}O_{16}S)_2Ba + C_{42}H_{76}O_{16}SBa$ ; silver salt,  $C_{42}H_{76}O_{16}SAg_2 + C_{42}H_{77}O_{16}SAg$ ; aluminium salt,  $(C_{42}H_{74}O_{16}S)_3Al_4$ .

The substances soluble in ether proved to be identical with the hydroxyoleic acids contained in the foregoing conjugated compounds. They are both crystalline, insoluble in water, readily soluble in ether, alcohol, carbon bisulphide, and benzene. *Hydroxyoleic acid*,  $C_{18}H_{34}O_3$ , melts at  $56-58^\circ$ ; the following salts have been analysed:—Normal copper salt,  $(C_{18}H_{33}O_3)_2Cu$ ; acid copper salt,  $(C_{18}H_{33}O_3)_2Cu + 2C_{18}H_{34}O_3$ ; acid barium salt,  $(C_{18}H_{33}O_3)_2Ba + 2C_{18}H_{34}O_3$ ; acid calcium salt,  $(C_{18}H_{33}O_3)_2Ca + 2C_{18}H_{34}O_3$ ; aluminium salt,  $(C_{18}H_{33}O_3)_6Al_2$ . *Trihydroxyoleic acid*,  $C_{18}H_{34}O_6$ , melts at  $64^\circ$ ; the following salts were obtained:—Copper salt,  $(C_{18}H_{33}O_5)_2Cu$ ; barium salt,  $(C_{18}H_{33}O_5)_2Ba + 2C_{18}H_{34}O_5$ ; aluminium salt,  $(C_{18}H_{33}O_5)_6Al_2$ ; silver salt,  $C_{18}H_{33}O_5Ag$ .

The reaction occurring in the manufacture of Turkey-red oil is therefore expressed by the equations—



In confirmation of this view, it was found that on heating sulphuric acid with oleic acid, hydroxyoleic acid was obtained, and that a mixture of glycerol, oleic acid, and sulphuric acid, when heated, yielded glycerol sulphate hydroxyoleate. Compounds similar to the last named were prepared by heating oleic and sulphuric acids with mannite, grape-sugar, starch, cellulose, or dextrin. They are all soluble in water, give metallic derivatives, and are decomposed when boiled with alkalis, with separation of hydroxyoleic acid.

A. J. G.

**Explosives and their Application.** (*Dingl. polyt. J.*, **248**, 509—513).—Dolliak attributes the presence of metal-dust in gun-powder to the wear and tear of the machines used for finely dividing and intimately mixing the powder.

Straw nitrocellulose is more unstable and therefore less secure than gun-cotton. This is due to the fact that although before nitrating the straw it is digested in a solution of potash, the cellulose of the straw fibre is not separated entirely in the pure state, but is contami-

nated with fat, wax, resin, or pectins, which form unstable nitro-compounds.

For the preparation of a new gun- and blasting-powder, Himly and Frützockler-Falkenstein grind and mix together the following substances in proportions so that when the mixture is ignited complete combustion occurs: nitre, potassium chlorate, and a solid hydrocarbon. The mixture is treated with a light hydrocarbon, and the plastic mass made into flat cakes, from which the liquid hydrocarbon is expelled by evaporation. The solid residue is then broken up into grains of the required size.

Reid recommends to moisten the explosive compound containing nitrocellulose with alcohol and dry it, whereby a hard and uniform mass is obtained.

It is stated that a determination of the heat produced and an estimation of the gaseous products formed by the combustion of an explosive, is not sufficient to show its value. The lead test in this case is said to give more accurate results. The active force of a variety of explosives was determined according to this test with the following results:—

	Proportion of hollow spaces in the lead test.	Active force according to trials made at the following places:—		
		St. Gothardt.	Ramsbeck.	Zankeroda.
Nitroglycerol.....	1000	—	—	—
Blasting gelatine....	1000	1000	1000	1000
Gelatine dynamite ..	770	—	—	730
Kieselguhr dynamite	700	698	683	688
Mercury fulminate ..	300	—	—	—

The following comparison by Steiner illustrates the working of a lignite coal mine with gunpowder and dynamite No. II, the total output being 50,000 tons:—

With the use of	Produce.				Current expenses, fl.	Working profit, fl.
	Tons at 2·60 fl.	Tons at 1·60 fl.	Tons without value.	Total for 50,000 tons fl.		
Gunpowder.....	39,400	7100	3500	113,800	80,500	33,300
Dynamite, No. II .....	31,600	9200	9200	96,880	74,000	22,880

These results confirm the fact that dynamite is less suitable than gunpowder for blasting coal, as its shattering effect is more powerful than that of gunpowder.

D. B.

## General and Physical Chemistry.

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**Separation of Rays of High and Low Refrangibility.** By F. v. ASSCHE (*Compt. rend.*, **97**, 838—840).—A thin layer of selenium, obtained by compressing a drop of the fused substance between plates of glass at 250°, and allowing it to cool slowly under pressure, only transmits the rays between Fraunhofer's lines A—C. The amount of absorption increases with the thickness of the layer. When a beam of white light is passed first through a solution of alum and then through a film of selenium, all the luminous rays are arrested. A thin film of selenium, if heated to 250°, is apparently opaque to all luminous radiation. C. H. B.

**Atmospheric Absorption by Aqueous Vapour.** By W. W. ABNEY and R. FESTING (*Proc. Roy. Soc.*, **35**, 328—341).—In the course of some investigations on the atmospheric absorption in the infra-red of the solar spectrum, the authors established the coincidence of the absorption-bands of the spectrum with those due to water. They have further confirmed Langley's researches as regards Cauchy's formula for refraction.

In this paper, the spectrum is examined, which is obtained by using the crater of the positive pole of the electric light as a source of radiation by means of a thermopile, and the variations produced by placing layers of water of different thickness in front of the slit. The diagrams show that the thermograms of the water spectra are absolutely coincident with the absorption in the photographs, but the former method is probably the more delicate.

By means of the thermograms, the solar temperature may be approximately estimated; for Dewar has shown that the temperature of the source of heat is nearly proportional to the square root of the total variation represented by the area of the thermogram curve. The temperature of the crater is calculated at about 6000, and in the prismatic solar spectrum the scale is 4·5 times that of the scale of the crater thermogram; the highest solar temperature, therefore, would be  $\sqrt{4\cdot5 \times 6000} = 12,700$ , a value far higher than that put forward by Siemens.

Among other results, the existence of a large quantity of solar radiation, due to low temperature, is shown to be more than probable. V. H. V.

**Radiant Matter Spectroscopy.** By W. CROOKES (*Proc. Roy. Soc.*, **35**, 262—271).—Whilst studying the phenomena presented by various substances when struck by the molecular discharge from the negative pole in a highly exhausted tube—the so-called radiant matter—the author observed a bright citron line or band: this appeared more markedly when the substance under examination was converted

into the sulphate by evaporation with strong sulphuric acid. Preliminary evidence tended to show that this band was due to calcium, for most native compounds of this element produced it, and it became better defined when solutions of these substances were precipitated by ammonium oxalate. But if the calcium compound gave no band originally, it could not be brought out by any process, chemical or physical. Tentative experiments established that this line was due to some member of the yttrium and its allied families present in samarskite, and by the method of differences these were ultimately restricted to the four following: mosandrum, lithium, ytterbium, and yttrium. By a long series of separations, this citron band was shown finally to be due to yttrium, whose sulphate in a "radiant matter" tube consists essentially of a broad red band, an intensely brilliant citron band, and two equally brilliant green bands.

The above investigations show that yttrium is more widely distributed than has been suspected hitherto. From the results of quantitative spectrum analysis it is seen that amongst other substances a specimen of coral contains 1 part of yttrium in 200 parts; strontianite, 1 part in 500; chondrodite from Mount Somma, 1 part in 4,000; calcite, 1 part in 10,000; ox-bone, 1 part in 10,000; a meteorite (Alfanello), 1 part in 100,000; and tobacco-ash, 1 part in 1,000,000.

V. H. V.

**Line Spectra of Boron and Silicon.** By W. N. HARTLEY (*Proc. Roy. Soc.*, **35**, 301—304).—Among other spark spectra of saline solutions, those of boron and silicon present a particular interest. In the spectrum of sodium diborate, three sharp lines  $\lambda$  3450.3,  $\lambda$  2497, and  $\lambda$  2496.3 appear, and if the solution of the salt be sufficiently strong, the sodium lines are not visible. A detailed description and the wave-lengths of the spark spectrum of silicon compounds are given, and it is noted that a certain group of these lines is attributed by Liveing and Dewar to the element carbon, although the author did not observe them in his spectrum of graphite. Probably the specimen of graphite used by Liveing and Dewar, although purified with the greatest care, contained traces of silicon, for not only graphite, but other elements, as aluminium and iron, are invariably contaminated with traces of silicon.

V. H. V.

**Ultra-violet Absorption Spectra of Albuminoids.** By J. L. SORET (*Compt. rend.*, **97**, 642—644).—Diluted white of egg albumin precipitated by hydrochloric acid and redissolved in excess,  $\beta$ -albumin dissolved in hydrochloric acid, purified albumin, protalbin, artificial protalbin, pepsino-pseudopeptone, pancro-pseudopeptone, casein from milk, serum from the blood of the pig, mucin from *Helix pomatia*, globulin, myosin, and syntonin all give practically the same spectrum, which is characterised by an absorption-band coincident with the cadmium line at 17, and a band of no absorption at 18. This fact indicates that all these albuminoids contain a common principle to which the absorption-band is due. Gelatin, which differs from albumin in other respects, is much more transparent to ultra-violet rays, and does not give the absorption-band.



Hydrochloric acid has no sensible effect on the character of the spectrum, but slightly diminishes the general absorption. Sodium hydroxide or ammonia, on the other hand, produces considerable alteration; the band of no absorption, coincident with the cadmium line at 18, disappears entirely; whilst the band at 17 remains unaltered or diminishes in intensity, and the curve from this point decreases regularly to the end of the spectrum. In many cases a faint absorption-band appears between 14 and 16; in others the band is reduced to a simple inflection. That is to say, the general absorption between 17 and 22 increases considerably, and the absorption-band becomes almost invisible and is displaced towards the more refrangible end. On neutralising the soda with hydrochloric acid, the original spectrum reappears without any sensible alteration. Sodium hydroxide alone is very transparent to this region of the spectrum. These results show that alkalis produce an alteration in the molecular constitution of albuminoids, and afford further proof that the latter contain a common principle.

Other organic bodies, such as sarcine and tyrosine, which combine with acids and bases, behave in a similar manner. Their spectra are not affected by hydrochloric acid, but are altered by alkalis, the change consisting in an alteration in the position of the bands or in their intensities, some of them disappearing altogether.

C. H. B.

**Production of Electricity by Evaporation, and Electrical Neutrality of Vapour arising from Electrified Surfaces of Liquids.** By L. J. BLAKE (*Phil. Mag.* [5], 16, 211—224).—Of the hypotheses proposed to explain the origin of atmospheric electricity, two have received considerable support among physicists, namely, the production of electricity by simple evaporation, and the convection of electricity upon the surface of any evaporating liquid.

In this paper the hypotheses are investigated experimentally by means of Kohlrausch's condenser with moveable plate, and an electrometer, which is described at length.

As regards the former hypothesis, the tabulated results indicate no production of electricity by simple evaporation. Similarly as regards the latter hypothesis, experiments on the evaporation of distilled water, sodium chloride solution, absolute alcohol, concentrated sulphuric acid, and sea water, showed that there is no convection of electricity from the electrified surface of a liquid when evaporating. In some experiments with sea water, the kind of electricity upon the surface of the condenser was of opposite sign to that of the water, whereas, had convection occurred, the reverse would have been the case.

In order to put the hypothesis to a favourable test, experiments were made with evaporating mercury, but with negative results, and thus it must be concluded that the vapour arising from electrified still surfaces of liquids is electrically neutral.

V. H. V.

**Effect of Temperature on the Electromotive Force and Resistance of Batteries.** By W. H. PREECE (*Proc. Roy. Soc.*, 35, 250—257).—As a continuation of former researches (cf. Abstracts,

1883, p. 840), the effect of an increase of temperature on the electromotive force and resistance of secondary batteries containing plates of lead and lead peroxide in sulphuric acid of various degrees of concentration. From an inspection of the tables and diagrams in the original paper, it is seen that the effect produced by heating the secondary batteries is the same in kind, but different in degree, from that on the Daniell cell. The E.M.F. practically remains constant, but the internal resistance diminishes with rise of temperature, increasing again as the temperature is lowered. Variations of strength of acid do not produce any very marked effect. The following short table illustrates the above remarks:—

Percentage of acid.	Resistance in ohms.		Decrease per cent.
	0°.	100°.	
10 .....	0·0752	0·046	61·0
20 .....	0·08	0·457	57·0
30 .....	0·062	0·0338	58·0
Mean .....	0·0724	0·425	59·6

V. H. V.

**Benzene as an Insulator.** By H. HERTZ (*Wied. Ann.*, **20**, 279—284).—Rowland and Nichols have established that in certain insulating crystals dielectric polarisation is not accompanied with the formation of any residual charge. They consider this latter phenomenon to be a necessary consequence of non-homogeneity of the insulating material. This view led the writer to examine a series of liquids, of which benzene is the most advantageous, as of a sufficient resistance and not giving any residual charge.

The apparatus used was practically a modification of a Leyden jar, in which the zinc plates, in circuit with a battery and electrometer, were the inner and outer coatings, and a layer of benzene the dielectric. The following phenomena were observed. At first the resistance was too small for measurement, and the residual nearly one-tenth of the original charge. After a short time these properties diminished *pari passu* until at the end of 24 hours the benzene became a perfect insulator, without any residual charge. The conductivity displayed at first by the benzene doubtless arises from impurities, and it is shown that the transference of the benzene from one vessel to another, or the introduction of the trace of any powder, will increase the conductivity of the benzene. On the other hand, the decrease of conductivity is due in part to the action of the current.

Electrically pure benzene seems to be the best approximation to an ideal insulating liquid, both as regards resistance and residual charge; its sole disadvantage is its volatility.

The residual charge, which makes its appearance in impure ben-

zene, arises from a subsequent polarisation, of whatever nature it may be, and not from an interpenetration of free electricity.

V. H. V.

**Electrical Resistance of Insulators.** By G. FOUSSEREAU (*Compt. rend.*, **97**, 996—998).—The resistances were determined in the manner previously described, by measuring the time required to charge a condenser at a given difference of potential across the particular substance. The resistance of porcelain varies with the temperature in the same manner as that of the more highly insulating varieties of glass: it is 751 at 60°, and 0.052 at 180°.\*

The resistance of sulphur, previously fused and then allowed to cool slowly in the prismatic condition, is 7.39 at 112.1°, and 3930 at 69°; below the latter temperature, the conductivity is inappreciable. When the same sulphur is allowed to remain at the ordinary temperature for some time, so that it devitrifies, its conductivity gradually increases: in one case the resistance after one day was 1170 at 17°; after two days, 705 at 17°. Octahedral sulphur shows no trace of conductivity at the ordinary temperature, and the conductivity only becomes appreciable at about 80°. It would appear from these facts that sulphur has a higher resistance when crystalline.

When sulphur melts, its resistance diminishes to one-fortieth its original amount. If the temperature is gradually raised from 114° to 150°, the resistance gradually diminishes as the temperature rises, and it varies between these limits in the ratio of 9 to 1. When the temperature rises to 160°, the sulphur becomes darker coloured and pasty, and its resistance increases. If the liquid is again cooled to the melting point, it retains a resistance higher than the original resistance, and the difference is greater the higher the temperature to which the sulphur has been heated, the longer it has been kept at this temperature, and the more quickly it has passed 155° in the process of cooling, this being about the temperature at which the inverse change takes place. By repeatedly heating the sulphur in this way to a high temperature, its original resistance at the melting point can be increased twelvefold.

When sulphur is allowed to cool in the prismatic form and is then remelted, it shows a diminished resistance at the same temperatures. Similarly, when octahedral sulphur is repeatedly crystallised in the prismatic form, its resistance at 115° is gradually reduced to one half. These results agree with Gernez' supposition that one variety of sulphur fully acquires the properties of another variety, only after repeated crystallisations.

The resistance of carefully dried ordinary phosphorus is 84,000 megohms at 15°, and 15,600 megohms at 42°; it is of the same order of magnitude as that of liquid sulphur. The resistance of liquid phosphorus is 2.32 megohms at 25°,† and 0.34 megohm at 100°.

C. H. B.

\* All the resistances except those of phosphorus are given in millions of megohms per cubic centimeter.

† This is the temperature given in the original paper. Apparently it should be 45°.

**A High Pressure Electric Accumulator.** By F. J. SMITH (*Phil. Mag.* [5], 15, 203—204).—Grove's gas battery cannot be conveniently used as an accumulator, or secondary battery, owing to the small quantities of gases contained in it. Its use may however be extended by storing the electrolytic gases under high pressure in a suitably constructed apparatus, such as the following. In a strong lead vessel, partly filled with 10 per cent. sulphuric acid, are enclosed platinised platinum cylinders in inverted tubes, the terminals being brought through insulating stoppers: with this arrangement a pressure of seven atmospheres can be easily used. It appears from preliminary experiments that the E.M.F. of this accumulator varies considerably with the pressure.  
V. H. V.

**Measurement of Electromotive Force.** By E. REYNIER (*Compt. rend.*, 97, 1056—1059).—The author measures the maximum electromotive force of a couple with a single electrolyte by means of a cell in which the active surface of the positive plate is 300 times that of the negative plate, and he measures the minimum electromotive force by means of a cell in which the surface of the negative plate is very much greater than that of the positive plate, the measurement in this latter case being made immediately after the battery has been working on short circuit for several hours. The maximum and minimum electromotive forces of several couples are given in a table.

The author concludes that the electromotive force of a couple with a single electrolyte must be regarded as the true electromotive force of the system, and its increase up to the maximum results from the addition of products formed by the action of the air. The effect of these products must not be confounded with the chemical energies due to the couple itself.  
C. H. B.

**Chemical Affinities in Terms of Electromotive Force.** By C. R. A. WRIGHT and C. THOMPSON (*Phil. Mag.* [5], 16, 25—48).

*On the E.M.F. of Clark's Cell.*—In this paper are described a series of experiments on the E.M.F. of Clark's cells ( $\text{Hg}|\text{Hg}_2\text{SO}_4|\text{ZnSO}_4|\text{Zn}$ ), compared with one another and with other cells, by means of the quadrant electrometer, so that they never generated any current, other than the minute leakage current. With cells constructed strictly in accordance with Clark's directions, a slight rise in E.M.F. was observed during the first few days, then the values became and remained constant. Increase of dilution of the zinc sulphate solution increased the E.M.F., whilst dissolved air produced no alteration; the presence of mercuric sulphate, in the form of turpeth mineral, caused a progressive decrease of the E.M.F., amounting to about 4 per cent. after 6–20 months. It was found that an increase of one degree in temperature produced a diminution 0.04 per cent. in the E.M.F.; and from the experiments with five cells described in this paper, it follows that between 2° and 27° the E.M.F. of the cell for any temperature  $t$  may be determined by the formula

$$1.457\{1 - (t - 15.5) \times 0.000041\} \text{ volt,}$$

assuming Clark's original valuation to be correct.

*On the Work done during Electrolysis.*—Previous researches by the authors have established that, when a current is passed through an electrolytic cell, the amount of energy expended in performing a given amount of electro-chemical work (apart from that transformed into heat) is not constant, but *increases algebraically with the current density*. In this connection, experiments by Favre appear to show that certain forms of electromotor cells can generate currents capable of doing more work externally to the cell than corresponds with the net chemical action, this extra work being gained at the expense of the sensible heat of the cell, which becomes cooled by the currents. Although Favre's results have been refuted by Weber, yet experiments described at length in the present paper point to the following results :—

(1.) When an electrolytic cell is of such a nature that the counter E.M.F. is negative, the E.M.F. developed is less the greater the density of the current generated. With small current densities, the E.M.F. has a maximum value, identical in some cases with the E.M.F. representing the algebraical sum of the chemical affinities involved ; in other cases the maximum E.M.F. is below that due to chemical action.

(2.) Some kinds of combinations, more especially those in which lead is the metal dissolved, develop a greater E.M.F. than that due to chemical action. Recent experiments of Braun (*Ann. Phys. Chem.* [2], 16, 561) confirm these general results, in proving that some combinations give an E.M.F. sensibly identical with that calculated from thermo-chemical data, whilst others fall short of and some exceed these values.

(3.) When the electrolytic cell is not an electromotor, the *counter E.M.F. increases in amount with the current density*. When the + electrode is of such a nature as to combine with the products of electrolysis, the rate of increase is slower the greater the chemical affinity between the so-called nascent products of electrolysis.

(4.) Whether the cell be an electromotor or not, there is always a greater or less degree of nonadjuvancy owing to the development of heat in place of electricity ; the particular extent to which this non-adjuvancy extends appears to be a complex function, not only of the chemical nature and physical condition of its surface, but also of the degree of concentration of the electrolyte.

When a gas is one of the permanent products of electrolysis, *the greater the surface condensing power of the material of the electrode, the less is the degree of non-adjuvancy.*

V. H. V.

**Conditions Affecting Area of Electrification.** By A. TRIBE (*Phil. Mag.* [5], 16, 90—95).—The areas of electrifications on an analysing silver plate in a solution of copper sulphate, can be determined by measuring the copper and silver peroxide respectively deposited on the plate ; the former gives the area of —, the latter that of the + electrification. The influence of strength of current, temperature, and strength of electrolyte is examined ; in all cases an inequality in the magnitude of the electrifications of opposite strength was observed ; generally the area of + electrification is the greater,

but with rise of temperature the relation is reversed. These experiments, taken in connection with others by the author on dissymmetry in the electrolytic discharge, in which it was inferred that the electromotive force on the + side of the trough is the greater, seem to be related to Faraday's observation that negative electricity discharges into the air at a somewhat lower tension than positive electricity; for if this be true of molecules of air, it is probably also true of molecules of other fluid media, as copper sulphate. A difference in the E.M.F. of the molecules in corresponding positions is therefore a feature of dissymmetry of certain electrolytic fields. This effect is observed in the phenomena mentioned above, viz., the differences in the area of like electrifications in analysing plates placed in corresponding positions.

V. H. V.

**Distribution of Electricity on Hollow Conductors in Electrolytes.** By A. TRIBE (*Phil. Mag.* [5], 16, 384—386).—It would *a priori* be concluded that the closest analogy exists between the distribution of electricity on hollow conductors in electrolytic and dielectric fields. In this paper this conclusion is confirmed experimentally.

Hollow silver tubes were placed in an electrolytic cell containing copper sulphate, midway between the electrolytes and perpendicular to them; through the cell a current of one ampère flowed for six minutes. It was found that the intermediate space of no electrification was far greater within than without the tube. Similarly the silver tube exerted a sort of protective action on a plate of silver enclosed within, but not in metallic connection with it. But in these experiments the area of + was always greater than that of — electrification (see preceding Abstract). Other experiments were also made, substituting tubes of wire gauze of various diameters for those of metallic silver, and a similar result arrived at. As foreseen, increase of diameter of tube decreases the power of protection from electrification.

V. H. V.

**Electrolysis of Sodium Chloride and its Industrial Applications.** By E. ROTONDI (*Gazzetta*, 13, 279—280).—The author's first experiments were made with a glass cylinder closed at bottom with parchment-paper and placed within a glass jar, both vessels containing a saturated solution of sodium chloride. On passing a current through the liquid, the positive pole of the battery being placed in the inner vessel, chlorine was there evolved, and hydrogen in the outer vessel, where also sodium hydroxide was formed, which was subsequently converted into carbonate by a stream of carbonic anhydride. In other experiments the inner vessel was made of porous earthenware—in others again of poplar wood. By these means solutions of sodium carbonate were formed, equal in strength to those obtained by Leblanc's process. In all the experiments, however, free chlorine was detected after a certain time in the inner vessel, its presence there being due to an alteration in the diaphragm. To avoid this inconvenience, the inner vessel was filled with distilled water, and the outer with a solution of sodium chloride, which was kept con-

stantly saturated. With this arrangement, the chlorine separated at the anode, being insoluble in the saturated solution, was evolved in the free state, and thus the alteration of the diaphragm and the formation of chlorinated compounds were avoided.

The electrolysis of sodium chloride in this manner may be utilised in several branches of industry, as in the bleaching of vegetable fibres, in calico-printing, &c., since by the expenditure of a moderate amount of mechanical power to generate the electric current, a powerful bleaching and oxidising agent may be obtained, together with caustic or carbonated alkali.

H. W.

**Relation between Radiation, Energy, and Temperature.** By W. W. ABNEY and R. FESTING (*Phil. Mag.* [5], 16, 234—229).—In this paper a series of determinations is quoted of the radiation and of the energy of incandescent lamps, when currents of varying strength were passed through the filaments. A Grove's battery was used as the source of energy, the intensity of which was measured by a tangent galvanometer, and the radiation of the lamp by a thermopile, whose surface was coated with lampblack. The lamps were heated in ovens heated to 300°, and the change of resistance measured directly by resistance coils.

The results obtained may be summed up thus: the *current* can be expressed as a function of the potential; the *radiation*, after a certain temperature has been reached, bears a simple proportion to the energy expended; the *resistance* can be formulated as a function of the energy, and therefore of the radiation; and the *temperature* appears to be a simple function of the resistance. The curves expressing the relation between the first two quantities, current and potential, can be represented by the equation  $c = ap + bp^{\frac{3}{2}}$ ; from this equation can be deduced another for the value of the energy in water,  $w = p^2(a + bp^{\frac{1}{2}})$ ; the resistance in ohms would be  $\frac{1}{a + bp^{\frac{1}{2}}}$ , whilst the form of the equation between energy and resistance is expressed thus:  $w = \left(\frac{1 - ar}{br}\right)^4 \times \frac{1}{r}$ .

Appended are the results of typical experiments with four different patterns of lamps, in which the dimensions of the carbon filaments differ considerably.

V. H. V.

**Heats of Combustion and Formation of Carbon Bisulphide and Carbonyl Sulphide.** By J. THOMSEN (*Ber.*, 16, 2616—2619).—The heat of combustion of liquid carbon bisulphide, according to Favre and Silbermann, is 258,400 c., or calculated for the gaseous condition, 264,800 c.; according to Berthelot's experiments, it is 253,300 c. The author's results both with carbon bisulphide and carbonyl sulphide, COS, are the following:—

Reaction.	Heat of combustion.	Reaction.	Heat of formation.
(CS <sub>2</sub> + O <sub>6</sub> ) .....	265,130 c.	(C,S <sub>2</sub> ) .....	— 26,010 c.
(COS + O <sub>3</sub> ) .....	131,010 „	(C,O,S) .....	+ 37,030 „
		(CO,S) .....	+ 8,030 „

The heat of combustion of carbon bisulphide in the liquid condition is 6400 c. less, and the heat of formation 6400 c. greater than in the gaseous state.

A. K. M.

**Heat of Formation of the Oxychlorides of Carbon, Phosphorus, and Sulphur.** By J. THOMSEN (*Ber.*, 16, 2619—2621).—The results are contained in the following table:—

Reaction.	Heat.	Reaction.	Heat.	Reaction.	Heat.
(C,O,Cl <sub>2</sub> )..	55,140 c.	(CO,Cl <sub>2</sub> )..	26,140 c.	(COCl <sub>2</sub> ,Aq) ..	57,970 c.
(P,O,Cl <sub>3</sub> )..	145,960 „	(PCl <sub>3</sub> ,O) ..	70,660 „	(POCl <sub>3</sub> ,Aq) ..	72,190 „
(S,O <sub>2</sub> ,Cl <sub>2</sub> ) ..	89,780 „	(SO <sub>2</sub> ,Cl <sub>2</sub> )..	18,700 „	(SO <sub>2</sub> Cl <sub>2</sub> ,Aq) ..	62,900 „

A. K. M.

**Heat of Formation of Pyrosulphuric Chloride.** By D. KONOWALOFF (*Ber.*, 16, 2629—2631).—This was determined from its heat of decomposition by potash solution (896·2 cal.). Calculated from this, its heat of formation is 188·2 cal., or calculated for the gaseous condition, 180·6 cal.

A. K. M.

**Heats of Solution and Hydration of the Alkaline Earths and the Alkalis.** By J. THOMSEN (*Ber.*, 16, 2613—2615).—The results are shown in the following tables, Berthelot's figures being given for comparison:—

*Heat of Solution of the Oxides and Hydrates.*

Reaction.	Thomsen.	Berthelot.
(BaO,Aq) .....	34,520 c.	27,880 c.
(SrO,Aq) .....	29,340 „	26,800 „
(CaO,Aq) .....	18,330 „	18,100 „
(BaO <sub>2</sub> H <sub>2</sub> ,Aq) .....	12,260 „	10,260 „
(SrO <sub>2</sub> H <sub>2</sub> ,Aq) .....	11,640 „	9,600 „
(CaO <sub>2</sub> H <sub>2</sub> ,Aq) .....	2,790 „	3,000 „
(KOH,Aq) .....	13,290 „	12,460 „
(NaOH,Aq) .....	9,940 „	9,780 „
(BaO <sub>2</sub> H <sub>2</sub> .8H <sub>2</sub> O,Aq) .....	—15,210 „	—
(SrO <sub>2</sub> H <sub>2</sub> .8H <sub>2</sub> O,Aq) .....	—14,640 „	—



*Heat of Hydration.*

Reaction.	Thomsen.	Berthelot.
(BaO, H <sub>2</sub> O).....	22,260 c.	17,620 c.
(SrO, H <sub>2</sub> O).....	17,700 „	17,200 „
(CaO, H <sub>2</sub> O).....	15,540 „	15,100 „
(BaO <sub>2</sub> , H <sub>2</sub> , 8H <sub>2</sub> O).....	27,470 „	—
(SrO <sub>2</sub> , H <sub>2</sub> , 8H <sub>2</sub> O).....	26,280 „	—

A. K. M.

**Densities of Solutions of Salts.** By C. BENDER (*Ber.*, **16**, 2556—2559).—From an examination of solutions of salts containing a number of gram-molecules to a litre, the author has arrived at a general law, according to which the density can be calculated from the number of gram-molecules of the anhydrous salt contained in a litre of the solution at a given temperature, namely, 15° and 18°. This depends on the supposition that an atom of an element (also certain groups of atoms) has a definite solubility value independent of the second atom or group of atoms with which it is united in a salt, as was shown by Valson (*Compt. rend.*, **77**, 806) in the case of moderately concentrated solutions. The author gives the following equation,  $d_{\mu} = d_{\mu(\sigma)} + \mu(m_b + m_a)$ , for determining the density of a solution,  $\mu$  being the number of gram-molecules of the salt,  $d_{\mu(\sigma)}$  the density of a solution of ammonium chloride containing the same number of gram-molecules to the litre,  $m_b$  the solubility value of the metal, and  $m_a$  that of the acid radicle. Water at 4° is taken as unity. The following is an example in which the density of a solution of copper nitrate at 15° is to be calculated:  $\mu = 3$ ,  $m_b = 0.0437$  (obtained from following table),  $m_a = 0.0163$ , and  $d_{\mu(\sigma)} = 1.0451$ . The calculated density is accordingly 1.2251, that found being 1.2250. The following values of  $m_b$  and  $m_a$  for different metals and acid radicles are in some cases only approximate:—

	At 15°.	At 18°.		At 15°.	At 18°.
NH <sub>4</sub> .....	0	0	$\frac{1}{2}$ Mg.....	0.0210	0.0221
K.....	0.0289	0.0296	$\frac{1}{2}$ Mn.....	0.0356	—
Na.....	0.0238	0.0235	$\frac{1}{2}$ Zn.....	0.0410	0.0410
Li.....	0.0078	0.0077	$\frac{1}{2}$ Cd.....	—	0.0606
$\frac{1}{2}$ Ba.....	0.0735	0.0739	$\frac{1}{2}$ Pb.....	0.1087	—
$\frac{1}{2}$ Sr.....	0.0500	0.0522	$\frac{1}{2}$ Cu.....	0.0437	0.0413
$\frac{1}{2}$ Ca.....	—	0.0282	Ag.....	—	0.1069
Cl.....	0	0	NO <sub>3</sub> .....	0.0163	0.0160
Br.....	0.0373	0.0370	$\frac{1}{2}$ (SO <sub>4</sub> ).....	0.0206	0.0200
I.....	—	0.0733	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .....	—0.0015	—

A. K. M.

**Critical Temperatures. II.** By B. PAWLEWSKI (*Ber.*, **16**, 2633—2636).—For first communication, see *Abstr.*, 1883, 276.

Substance.	(T.)	(t.)	(T - t.)
Phosphorus trichloride .....	285·5°	75·5°	210·0°
Tetrachlormethane .....	285·3	75·4	209·9
Ethylene chloride..... (about)	283·0	85·0	198·0
Ethylidene chloride .....	254·5	57·8	196·7
Allyl chloride .....	240·7	45·5	195·2
Ethyl bromide .....	236·0	39·0	197·0
Methylal.....	236·6	43·0	180·6
Ethylal .....	254·4	104·3	150·1
Triethylamine .....	267·1	90·1	177·0
Isopentane .....	194·8	31·0	163·8
Amylene.....	201·0	38·0	163·0
Hexane .....	250·3	68·0	182·3
Diallyl.....	234·4	59·1	175·3
Diisobutyl .....	270·8	107·5	163·3
Octylene.....	298·6	123·6	175·0
Toluene .....	320·8	111·0	209·8
Butyl alcohol.....	287·1	117·2	169·9
Trimethylcarbinol.....	234·9	83·0	151·9
Isopentylalcohol .....	306·6	132·1	174·5
Ethyl crotonate .....	326·0	138·8	187·2
Ethylpropyl ether.....	233·4	63·9	169·5
Allylethyl ether.....	245·0	67·2	177·8
Acetic acid.....	321·5	118·5	203·0
Propionic acid .....	339·9	138·5	201·4

The author disputes some points in connection with Nadejdine's law (*Beiblätter, z. Ann. Phys. Chem.*, 1883, 678). A. K. M.

**Influence of Pressure on the Temperature of Volatilisation of Solids.** By W. RAMSAY and S. YOUNG (*Proc. Roy. Soc.*, **35**, 308—310).—Experiments were undertaken in order to ascertain whether solids have definite volatilising points under different pressures, and whether these pressures are identical with their vapour-tensions. A solid has a limited surface, which cannot on heating be increased by formation of bubbles; it would *à priori* be expected that increasing the supply of heat, the temperature of the solid would rise until a temperature is reached at which the rate of evaporation is equivalent to the rate at which heat is communicated to it. By such reasoning, the existence of hot ice was maintained by Carnelley and others.

If, then, the rate of evaporation at the surface of a solid is independent of the extent of that surface, but influenced only by the rate at which heat is communicated to it, and as in the case of liquids, by the pressure to which it is exposed, it follows that solids have definite temperatures of evaporation, corresponding to definite pressures, as liquids have definite boiling points. Experiments with ice and camphor show that these pressures are sensibly the same as the maximum tensions of the vapours of these solids at corresponding temperatures.

In the case of ice, the maximum temperature attainable under any given pressure is indicated by Thomsen's ice-steam line.

V. H V.

**Nature of Solution.** By W. W. J. NICOL (*Phil. Mag.* [5], 15, 91—101).—The phenomenon of solution is usually explained by the formation of a hydrate, more or less stable, of the substance to be dissolved, this hydrate diffusing throughout the mass of the liquid with production of a homogeneous solution. But this hypothesis fails to explain the alteration in the solubility of salts when simultaneously dissolved, the greater or lesser solubility of various salts, and the greater or lesser increase of solubility of salts with rise of temperature. Further, the experiments of Wiedemann and of the author on sodium sulphate tend to prove that the crystalline salt parts with its water of crystallisation at 34°, whether in solution or not. Thus the dilemmas arise of an explanation of solution by hydration, and increased solubility by diminished hydration, whilst an example of a salt is offered, which dissolves in the anhydrous state, and is then less soluble than when hydrated.

In this paper the following hypothesis is brought forward: the solution of a salt in water is a consequence of the attraction of the molecule of water for a molecule of salt, exceeding that of the molecules of the salt for one another. At the saturation point, the attraction of dissimilar molecules is counterbalanced by that of similar molecules.

This hypothesis receives experimental support, not only from Kremer's researches on the influence of the temperature at which crystallisation takes place, on the sp. gr. of the salt, but also by Berthelot's determinations on the heats of solution of various salts before and after fusion. The latter has established that the solution of that form of salt which crystallises at ordinary temperatures, is attended by absorption of heat, due to the heat absorbed by the liquefaction of the salt exceeding that of its combination with water; or in other words, the work to be done in separating the molecules of salt requires a greater expenditure of energy in the form of heat than that given out by the union of the water with the salt.

Again, in most cases the volume of the solution is usually less than the sum of the volumes taken together of the salt and water before solution. In this connection the experiments of Gerlach show that the amount of contraction does not increase regularly as the amount of salt dissolved increases. This is in accordance with the theory enunciated above, that the greater the amount of salt already in solution, the less is the result of the attraction of dissimilar, but the greater that of similar molecules.

Again determinations by Gerlach and Kremer on the coefficient of expansion of salt-solutions have proved that for weak solutions of salts the coefficient of expansion is in most cases greater than that of water; and the same obtains with strong solutions up to a certain temperature. In a solution, the effect of heat on the attraction of water for water, and of water for salt, will be to produce expansion, but on the attraction of salt for salt, to produce contraction. In dilute solution this last need not be considered, so that the net result is an

expansion due not only to that of water, but also to the attraction of the water for the salt. If this theory be correct, it will be possible to connect together the molecular volume of solids and their solubility.

V. H. V.

**Solubility of Salts in Water at High Temperatures.** By W. A. TILDEN and W. A. SHENSTONE (*Proc. Roy. Soc.*, **35**, 345—346).—This paper contains a brief description of experiments made with a view of determining the solubility of salts in water at temperatures above its boiling point.

As a general result it may be stated that solubility and fusibility are phenomena intimately connected: for increase of solubility consequent on a rise of temperature above  $100^{\circ}$  is the greatest in the most fusible, and least in the least fusible. If the results are represented graphically, taking for abscissæ degrees of temperature, and for ordinates the quantities of salt dissolved in 100 parts of water, then the higher the melting point, the more nearly the curves approximate to a straight line.

These relations can be illustrated by potassium chlorate and potassium haloïd salts. As regards sodium sulphate, the solubility increases from  $6-34^{\circ}$ , the melting point of the decahydrated salt,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ; then the solubility diminishes until a temperature of  $120^{\circ}$  is reached. From  $120^{\circ}$  to  $140^{\circ}$  there is no appreciable change, but at  $160^{\circ}$  there is a notable increase of solubility, which is still further increased at  $180^{\circ}$  and again at  $230^{\circ}$ .

*Parts by Weight of Anhydrous  $\text{Na}_2\text{SO}_4$ , dissolved by 100 parts of Water at*

$0^{\circ}$ .	$34^{\circ}$ .	$100^{\circ}$ .	$120^{\circ}$ .	$140^{\circ}$ .	$160^{\circ}$ .	$180^{\circ}$ .	$230^{\circ}$ .
5	78.8	42.7	41.95	42	42.9	44.25	46.4

In view of these facts the act of solution can no longer be explained by the formation of hydrates of the dissolving salt. V. H. V.

**General Law of the Freezing of Solvents.** (*Compt. rend.*, **97**, 825—831.)—A report by Cahours, Berthelot, and Debray on Raoult's memoir. (See Abstr., 1882, p. 1260; 1883, p. 278.) C. H. B.

**Freezing Point of Alkaline Solutions.** By F. M. RAOULT (*Compt. rend.*, **97**, 941—943).—The following results were obtained:

Base.	Mol. weight.	Reduction in freezing point caused by 1 gram of the base in 100 grams of water.	Mol. reduc- tion.
Barium hydroxide .....	171·0	0·290	49·7
Strontium „ .....	121·5	0·396	48·2
Calcium „ .....	74·0	0·648	48·0
Lithium „ .....	24·0	1·558	37·4
Sodium „ .....	40·0	0·905	36·2
Potassium „ .....	56·0	0·630	35·3
Thallium „ .....	221·0	0·150	33·1
Cæsium „ .....	149·6	0·237	35·5
Rubidium „ .....	102·4	0·360	36·9
Tetramethylammonium hydroxide	91·0	0·404	36·8
Trimethylethylammonium „	105·0	0·353	37·1
Ammonia .....	17·0	1·117	16·9
Methylamine .....	31·0	0·638	19·8
Trimethylamine .....	59·0	0·342	20·2
Ethylamine .....	45·0	0·411	18·5
Propylamine .....	59·0	0·312	18·4
Aniline .....	93·0	0·164	15·3
Nicotine .....	162·0	0·124	20·2

It is evident that in accordance with the general law, soluble bases may be divided into two classes, one of which gives a molecular reduction between 33 and 48 (mean = 39), whilst the other gives a molecular reduction between 16 and 20 (mean = 19), or practically one-half. The differences between the molecular reductions of individual members of each group are considerably greater than in the case of acids. The first group may in fact be divided into two sub-groups: one containing the hydroxides of dyad metals with a molecular reduction of about 48, and the other the hydroxides of monad metals with a molecular reduction of about 35.

Berthelot, Menschutkin, and the author have previously shown that potash and soda displace ammonia, methylamine, ethylamine, triethylamine, trimethylamine, and aniline almost completely from their salts in dilute alcoholic solution. The author also finds that barium hydroxide and rubidium hydroxide displace ammonia completely from ammonium chloride, and that trimethylethylammonium hydroxide displaces ammonia almost completely from ammonium iodide. Hence it may be said that any member of the first group can almost completely displace any member of the second group from its salts in dilute solution. A similar relation has been found to hold in the case of the two groups of acids, and it may be stated as a general law that strong acids and strong bases in solution in water produce the normal molecular reduction of the freezing point (about 40), whilst feeble acids and feeble bases produce the abnormal molecular reduction (about 20). It is worthy of note that all the organic acids and bases, with the exception of the hydroxides of organic ammonias, are found in the second group. The relation which exists between the chemical energies of acids and bases and the molecular reduction in the freez-

ing point of water, does not however hold good in the case of all solvents. In the case of certain solvents, acetic acid for example, strong acids, such as sulphuric and hydrochloric acids, produce only half the reduction in freezing point which is produced by weak acids, such as benzoic acid and phenol. The relation observed in the case of water is probably due to the fact that the strong acids and bases have a greater attraction for water, and therefore their molecules are more completely separated by solution, whilst the weak acids and bases have very little attraction for water, and their molecules consequently remain united together after solution, most probably in pairs. This latter supposition would explain the fact that they produce only half the normal molecular reduction.

C. H. B.

**Perfect Elasticity of Solid Bodies : a New Relation between Solids and Liquids and Gases.** By W. SPRING (*Ber.*, 16, 2723—2728).—The author has subjected a large number of metals and metallic salts to a pressure of 20,000 atmospheres, and determined their density before and after the operation. As a rule no alteration in density and, consequently, no permanent change in volume, is produced by the pressure, excepting that due to cavities in the solids. If the solid is capable of existing in a denser allotropic modification, then a permanent compression ensues.

When a bar of metal is bent, the concave portion experiences pressure and the convex undergoes expansion. If the bar remains curved after the force which altered its shape is removed, the result is due to a passage of matter from the concave to the convex side. The limit of elasticity of a solid is the critical moment at which the particles begin to "flow" under the influence of the forces exerted on them.

A body is brittle when its particles no longer have the power of "flowing" under pressure.

W. C. W.

**Determination of Atomic Weights by Means of Metallic Sulphates. Atomic Weights of Copper, Zinc, and Nickel.** By H. BAUBIGNY (*Compt. rend.*, 97, 854—856, 906—908, 951—954).—The principal source of error in previous determinations of the atomic weights of metals by means of their sulphates has been the difficulty of expelling the last traces of free acid and moisture without at the same time partially decomposing the sulphate. The author finds that all sulphates, with the exception of those of gold and the platinum metals, may be heated for several days at 440°, the temperature of boiling sulphur, without undergoing any decomposition, and that, even at this high temperature some sulphates lose the last traces of free acid very slowly. By this method the preparation of sulphates in a definite form is easier than the preparation of chlorides. Ferric sulphate, for example, can readily be obtained quite pure as a white salt with a pinkish tinge. The normal anhydrous sulphates thus obtained can be completely converted into oxides by heating them at a high temperature in a platinum boat placed inside a platinum tube heated by a muffle, one end of the tube being open to the air. The use of the platinum tube renders it easy to ascertain whether any spirting has taken place, and also protects the oxide

from the reducing gases of the furnace. In an actual determination, the purified sulphate is placed in a weighed platinum boat, and the latter is placed inside a glass tube which is heated in sulphur vapour until the sulphate ceases to lose weight. The boat with its contents is then put inside the platinum tube in the muffle and heated until all the acid is expelled. After the residual oxide has been weighed, it is dissolved in hydrochloric acid and the solution tested with barium chloride. This method is of course inapplicable to sulphates which volatilise without decomposition, or to sulphates which yield oxides which are volatile at high temperatures, like those of barium and strontium. In such cases the synthetical method must be adopted, the last traces of water and free acid being expelled by heating at  $440^{\circ}$ .

The atomic weights given below have been calculated on the assumption that the atomic weight of oxygen is 16.

*Copper*.—Pure metallic copper or pure artificial atacamite was dissolved in dilute sulphuric acid, and the solution carefully evaporated. Determinations were made with the first crop of crystals, and also with the residue obtained by evaporating the mother-liquor left after the separation of a second crop of crystals. The mean of the determinations is  $\text{Cu} = 63.468$  if  $\text{S} = 32.074$ , or  $\text{Cu} = 63.396$ , if  $\text{S} = 32$ .

*Zinc*.—Distilled zinc was treated with a quantity of sulphuric acid insufficient to dissolve it, and the filtered solution was evaporated to dryness. The residue was heated at  $440^{\circ}$ , dissolved in water, a portion of the zinc precipitated by hydrogen sulphide, and the liquid digested with the precipitate for some time in order to remove cadmium, lead, &c. The liquid was then filtered, the zinc precipitated as sulphide, the precipitate washed with very dilute sulphuric acid, and then dissolved in sulphuric acid, and the solution evaporated. The mean of the determinations is  $\text{Zn} = 65.403$  if  $\text{S} = 32.074$ , or  $\text{Zn} = 65.334^*$  if  $\text{S} = 32$ .

*Nickel*.—The commercial nitrate was very carefully purified, and was eventually converted into the anhydrous sulphide by saturating a solution of the sulphate with hydrogen sulphide, and heating it in closed vessels at  $100^{\circ}$ . The nickel sulphide thus obtained was dissolved in aqua regia and the solution evaporated with excess of sulphuric acid. Nickel sulphate obstinately retains traces of free acid even at  $440^{\circ}$ , and prolonged heating is necessary in order to obtain it perfectly pure. The monoxide left on ignition of the sulphate has no tension of dissociation at the melting point of gold, even in a vacuum. The mean of the determinations is  $\text{Ni} = 58.748$  if  $\text{S} = 32.074$ , or  $\text{Ni} = 58.678$  if  $\text{S} = 32$ . C. H. B.

**Molecular Weight of the Amines: Trimethylamine.** By J. DEWAR and A. SCOTT (*Proc. Roy. Soc.*, **35**, 347—349).—The substituted ammonias are peculiarly fitted to reveal the small differences from whole numbers in the conjoint values of atomic weights of carbon and hydrogen. By selecting amines of sufficiently high

\* *Note by Abstractor*.—This number is identical with that recently obtained by Marignac (*Zeitsch. Anal. Chem.*, 1884, 133).

molecular weights, butylamine for example, it is possible to integrate these small positive and negative increments: and, theoretically, it should be possible to ascertain whether the atomic weight of hydrogen differs from unity, when  $O = 16$  is taken as the standard, provided the atomic weight of carbon be accepted as sufficiently well defined by independent investigations. The crude base was transformed into tetrethylammonium bromide, decomposed by dry distillation, separated from the chloride with potassium hydroxide, and fractionally distilled. The portion boiling between  $90-91^{\circ}$  was treated with nitrous acid to eliminate traces of the primary and secondary amines, and finally converted into the bromide. The relation between this salt,  $Et_4NHBr$ , and silver was then determined, and the average result of fairly concordant experiments gave as the molecular weight of the bromide 182.012. The value for triethylammonium is 102.061; and if from this be subtracted Stas' value for ammonium, 18.074, the resultant, 83.987, is the molecular weight of the hydrocarbon  $C_6H_{12}$ .

These results are sufficient to prove that if the atomic weight of hydrogen be taken as unity, the atomic weight of carbon is 12, and thus the addition of 6 atoms of carbon to 12 of hydrogen results in a compound, whose molecular weight is the integer 84. But this value may be due to the summation of positive and negative variations from the respective values 12 or 1 respectively.

This investigation will be continued, and Schützenberger's hypothesis on the variability of the atomic weight of carbon will be made the subject of a future discussion.

V. H. V.

**Demonstration of the Increase of Weight of Bodies on Combustion.** By M. ROSENFELD (*Ber.*, 16, 2753—2758).—In order to show the increase in weight which potassium, sodium, magnesium, tin, foil, sulphur, carbon, and a taper undergo on combustion, the author employs a Nicholson's areometer instead of a balance.

In the experiment with tin foil, it is necessary to affix a thin iron or brass wire (25 cm. long) across the pan of the areometer. The tin foil hangs on each end of this wire.

For sulphur and charcoal, a small tube containing soda-solution is used. The tube is closed by a cork through which two narrow tubes pass; the longer tube dips into the soda. The sulphur or charcoal and the absorption tube are placed on the scale of the areometer. The sulphur is then brought into a hard glass tube, through which oxygen is passed. The tube is heated, and the products of combustion are passed into the absorption tube, which is again placed on the areometer after the experiment. A somewhat similar arrangement is used in the case of the taper.

W. C. W.

**Lecture Experiments.** By M. ROSENFELD (*Ber.*, 16, 2750—2752).—1. The preparation of mercuric oxide may be shown by heating potassium amalgam at  $225^{\circ}$  in a long-necked flask. The flask is closed by a cork through which two tubes are inserted. One tube dipping down to the surface of the mercury is connected with a gasometer filled with oxygen. Through the second tube, the excess of



oxygen escapes into a cylinder filled with water, standing in a pneumatic trough.

II. Zinc oxide is prepared by melting about 40 grams of zinc in a flat evaporating basin. A small piece of sodium is added, and a current of air is forced on the surface of the metal.

III. To obtain nitrogen from the air, the author recommends that the oxygen should be removed by means of a sheet of burning tin-foil.

W. C. W.

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## Inorganic Chemistry.

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**Purification of Hydrochloric Acid.** By E. BENSEMANN (*Arch. Pharm.* [3], 21, 291).—Hydrochloric acid can be entirely freed from arsenic by diluting it with water, adding potassium chlorate in small quantity, and warming the liquid. On distilling this mixture, hydrochloric acid free from arsenic is obtained, but of course it contains free chlorine. W. R. D.

**Some Reactions of Ozone.** By A. WAGNER (*Zeits. Anal. Chem.*, 22, 316—318).—On placing a piece of filter-paper, soaked in a boiling ethereal solution of anthracene, in a bottle containing phosphorus partially covered with water, anthraquinone is formed. Similar treatment causes aniline hydrochloride to turn brown, whilst exposure to air through which strong electric sparks are passing, produces a reddish-brown colour. In like manner diphenylamine gives a deep brown when the ozone is produced by phosphorus, and a lemon-yellow when the electrical discharge is used. Diphenylamine-sulphonic acid similarly treated becomes blue, passing into green in the former case, and deep blue in the latter. P. F. F.

**Colour of Water.** By W. SPRING (*Bied. Centr.*, 1883, 289—291).—Fresh distilled water in tubes 5 metres  $\times$  4 cm. appears of a sky-blue colour, which however changes after a few hours to a pale green; but if 0.0001 of mercuric chloride is added to the original water, no change occurs; if it be added to the green water, a blue-green tint is obtained, but never the original colour; it is therefore concluded that the change from blue to green is effected by minute organisms. A beam of light sent through the column of water is invisible (laterally?), consequently the colour is natural to the water and not to reflection from minute particles. Amyl and ethyl alcohol, and acetic acid are colourless. Pure blue water treated with lime and then with carbonic anhydride appeared at first black, changing to brown, yellow, and green; similar results were obtained with baryta-water containing free silicic acid and sodium silicate. The final conclusions drawn are:—light does not pass through a thick layer of water containing solids in suspension; the yellow colour is due to suspended matter, or to that matter forming a saturated solution; as carbonates are

deposited, the colour approaches more nearly to blue. In natural blue waters, calcium and magnesium carbonates, silica and alumina are in solution; whilst in the green they are partly undissolved through a deficiency in the carbonic anhydride. In the blue Rhine we have 786  $\text{CaCO}_3$  and 79.5  $\text{CO}_2$ , whilst in the green Rhine 1056  $\text{CaCO}_3$  and 76  $\text{CO}_2$ .  
E. W. P.

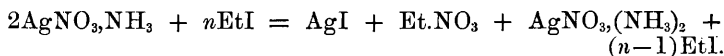
**Hydrated Carbon Bisulphide.** By F. P. VENABLE (*Amer. Chem. J.*, 5, 15—19).—The author confirms Ballo's statement that the white substance obtained by the rapid evaporation of carbon bisulphide is a hydrate, as it cannot be formed in dry air under conditions similar to those in which it is readily formed in moist air. The temperature of  $-12^\circ$ , given by Wartha as that of its formation or decomposition, does not appear to be correct. (For previous experiments on this subject see *Watts's Dictionary*, Suppl. 2, 264.)  
A. J. G.

**Modification of Noack's Method of Preparing Carbonic Oxide.** By L. P. KINNICUTT (*Amer. Chem. J.*, 5, 43—44).—Noack has recently shown that carbonic oxide can be prepared by passing carbonic anhydride over heated zinc-dust (*Ber.*, 16, 75). It may however be prepared more conveniently by heating a mixture of magnesite with twice its weight of zinc-dust. After the first five minutes, the gas is nearly pure carbonic oxide.  
A. J. G.

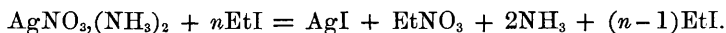
**Manufacture of Phosphoric Acid.** By E. W. RUNYON (*Pharm. Journ.* [3], 14, 48).—The preparation of phosphoric acid free from arsenic has hitherto been a matter of difficulty, as commercial phosphorus is always contaminated with arsenic, which is not removed in the ordinary process of oxidation by nitric acid. It has been proposed to remove the arsenic from the acid thus prepared by hydrogen sulphide, but the author finds that owing to the long time occupied in removing every trace of arsenic, this method is not a practicable one. He recommends the process proposed by Wenzell, which depends on the aerial oxidation of the phosphorus by exposure in trays in presence of water: full details of the apparatus used are given in the paper. The solution of phosphorous acid obtained is heated, whereupon the arsenic separates in the metallic condition, and after being kept at a temperature of about  $190^\circ$  for 30 minutes, the separation is complete. This liquid (sp. gr. 1.75) is diluted with an equal bulk of water, filtered through paper, and oxidised by nitric acid in the ordinary way.  
W. R. D.

**Borax in California.** By AYRES (*Arch. Pharm.* [3], 21, 297).—The borax imported from California is principally obtained from two lakes, Borax Lake and Clear Lake, which are about 80 miles north of San Francisco. Borax Lake is about three-quarters of a mile long, and has an average depth of four feet. Crystals which were taken from the mud at the bottom were found to be pure sodium pyroborate; 1.077 gram of total solid residue were yielded by 30 grams of the water. This residue contained 0.618 gram of sodium carbonate, 0.204 gram of sodium chloride, and 0.178 gram of borax.  
W. R. D.

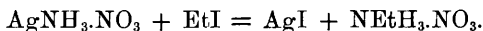
**Silver Nitrate and Ammonia.** By A. REYCHLER (*Ber.*, 16, 2421—2424).—Monammonia silver nitrate,  $\text{AgNO}_3\cdot\text{NH}_3$ , was described by the author (Abstr., 1883, 902) as a nitrate of argentammonium, a view which is found to be incompatible with the behaviour of this compound when treated with ethyl iodide. Ethyl iodide reacts with it at the ordinary temperature, heat being evolved, and silver iodide, ethyl nitrate, and diammonia silver nitrate formed, thus:—



The diammonia silver nitrate is also acted on by ethyl iodide, with formation of silver iodide, ethyl nitrate, and ammonia, thus:—



Some ethylamine is also produced by the action of the ammonia on the ethyl nitrate and ethyl iodide. If monammonia silver nitrate were a derivative of argentammonium, then ethyl iodide would react with it, so as to form ethylamine nitrate, as follows:—



But in light of the above reactions, the author is inclined to regard monammonia silver nitrate either as a molecular compound of ammonia with silver nitrate, or as a compound having the following constitution:  $\text{OH}\cdot\text{NO}(\text{NH}_2)\cdot\text{OAg}$ .  
P. P. B.

**Atomic Weight of Beryllium.** By J. E. REYNOLDS (*Proc. Roy. Soc.*, 35, 248—250).—Although specimens of beryllium used for determinations of the specific heat of the metal were impure, yet the results are all in one direction, that is, indicating apparent gain in specific heat with increased purity of material. The spectroscopic evidence of Hartley (*Trans.*, 1883, 316) shows that beryllium is the first member of a dyad series of elements, of which calcium, barium, and strontium are probably homologues. Thus two independent methods of research tend to prove that the atomic weight of 9.2 is the more correct, and that beryllium is the first member of Mendeleeff's second series of elements.  
V. H. V.

**Reply to the Above Paper.** By T. S. HUMPHIDGE (*Proc. Roy. Soc.*, 35, 358—359).—In this paper, exception is taken to the statement of Reynolds that the results of determinations of the specific heats of beryllium are higher, the less the proportion of impurities. But even admitting this, it is hardly probable that the specific heat of the fused metal could be 50 per cent. greater than that of the crystalline metal. The author has prepared purer samples, analyses of which are promised. As regards the observations of Hartley, the slight spectroscopic resemblance between beryllium and the alkaline earth-metals can hardly outbalance all the weighty chemical and physical differences between them; and even if beryllium is a dyad, its nearest homologues are decidedly magnesium and zinc, not calcium, strontium, and barium.  
V. H. V.

**Diffusion of Didymium.** By A. COSSA (*Gazzetta*, **13**, 280).—This metal, besides being found in apatites, scheelite, and various kinds of limestone, occurs in large quantity in the sphene of the syenite of the Biellese and of the Collegno limestone. The frequent association of didymium-compounds with those of calcium in homogeneous and perfectly crystallised minerals is regarded by Cossa as a confirmation of his opinion, that didymium, at least in compounds in which it is associated with calcium, may be regarded as a bivalent metallic radicle.

H. W.

**Magnesium Bromide and Iodide.** By O. LERCH (*J. pr. Chem.* [2], **28**, 338—356).—Although magnesium bromide has been prepared by the action of bromine vapour on a strongly heated mixture of carbon and magnesium oxide, it could never, owing to its non-volatility, be purified and analysed. The author has observed that bromine vapour combines directly with magnesium with the greatest readiness at a very high temperature, namely, at the melting point of the metal. By heating small pieces of magnesium in a vertical hard glass tube before the blowpipe, so that only the lower end of the tube is heated, and admitting bromine vapour by a smaller tube passing through the magnesium almost to the bottom of the larger tube, magnesium bromide may be obtained in quantity. The greatest caution is required in this dangerous operation. *Magnesium bromide* is a white crystalline mass, having the appearance of magnesium chloride. It is easily oxidised on exposure to air, is not volatile, and is more hygroscopic than the chloride. Analysis agrees with the formula  $\text{MgBr}_2$ ; but owing to the action of this metal on glass at a high temperature, the estimated quantity of bromine is slightly lower than that calculated. The salt was also obtained by evaporating a solution of hydrated magnesium bromide and ammonium bromide to dryness, and driving off the latter by heat; also by melting anhydrous magnesium chloride with ammonium bromide.

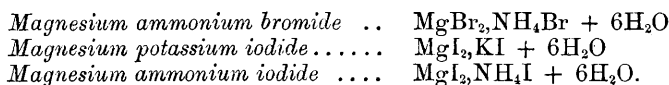
*Magnesium Iodide.*—This salt was also obtained by heating pieces of magnesium in a vertical tube to the melting point, and adding slowly small quantities of iodine; the reaction takes place with great violence. The iodide sinks below the molten metal, and also somewhat attacks the glass. It has the same appearance as the bromide, but melts at a higher temperature, and is more readily oxidised on exposure to the air. Analysis agrees with the formula  $\text{MgI}_2$ . The salt was also obtained from hydrated magnesium iodide and ammonium iodide, and by melting magnesium chloride with ammonium iodide.

*Hydrated magnesium bromide* is obtained by the action of bromine on magnesium dust and water. Crystallised over sulphuric acid, it is obtained in hygroscopic crystals, and analysis agrees with the formula  $\text{MgBr}_2 + 6\text{H}_2\text{O}$ .

*Hydrated magnesium iodide*, obtained in a similar way to the above, has the formula  $\text{MgI}_2 + 8\text{H}_2\text{O}$ .

*Magnesium potassium bromide* was formed by adding to a known quantity of hydrated magnesium bromide sufficient potassium bromide to form the double salt  $2(\text{KBr}),\text{MgBr}_2 + 6\text{H}_2\text{O}$ , as mentioned by

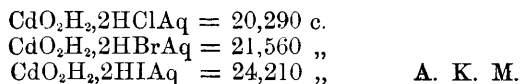
Löwig (*Repert.*, **29**, 261). On evaporating the solution over sulphuric acid, potassium bromide containing only 2 per cent. magnesium bromide crystallised out at first, and for some time after crystals containing no definite quantity of magnesium bromide were obtained; finally, however, a salt was obtained of a composition similar to that of carnallite,  $\text{KCl}, \text{MgCl}_2 + 6\text{H}_2\text{O}$ . Analysis agreed with the formula  $\text{KBr}, \text{MgBr}_2 + 6\text{H}_2\text{O}$ . A deficiency of over 2 per cent. of bromine was observed; but on analysis of carnallite prepared by crystallisation from its mother-liquor, there was a similar deficiency of chlorine, probably owing in both cases to the difficulty of purifying the very deliquescent crystals.



The halogen compounds of magnesium are similar in their behaviour towards water, in melting only at a high temperature, and in solidifying to crystalline masses; they differ in their behaviour to the air, for whilst the chloride is but slowly decomposed at the melting point, the bromide is more easily decomposed and the iodide with great rapidity at ordinary temperatures. The hydrated and double salts show the same characteristics respectively as do the halogen compounds. The author purposes continuing his investigation.

A. B.

**Cadmium Oxide.** By J. THOMSEN (*Ber.*, **16**, 2616).—The author has shown that hydrochloric, hydrobromic, and hydriodic acids exhibit the same heat of neutralisation with sodium hydroxide in aqueous solution, and that practically the same result is obtained when the above acids are neutralised with baryta, magnesia, zinc oxide, and copper oxide. Cadmium oxide is distinguished from the magnesium group by many of its chemical properties, and by its heat of neutralisation, which is greater for hydrobromic than for hydrochloric acid, and greater for hydriodic than for hydrobromic acid: in this respect it bears more resemblance to the heavy metals:—



**Spontaneous Oxidation of Mercury.** By D. MACALUSO (*Gazzetta*, **13**, 485—489).—The author has shown, by a series of careful experiments, that mercury is not oxidised by exposure to pure dry air or to pure aqueous vapour, but that in a mixture of the two, oxidation takes place, with production of the well-known grey pellicle of suboxide. This action is analogous to the formation of mercurous chloride when mercury is left in contact with gaseous hydrogen chloride or its aqueous solution in presence of air, whereas in pure hydrogen chloride, or its pure aqueous solution perfectly deprived of air, no such formation takes place.

H. W.

**Double Fluorides and Oxyfluorides of Titanium.** By A. PICCINI (*Compt. rend.*, **97**, 1064—1067).—When an aqueous solution of titanium trichloride is added gradually to a concentrated solution of ammonium fluoride, or, better, when a solution of the normal fluotitanate in a solution of ammonium fluoride is reduced by electrolysis, the compound  $\text{TiF}_3 \cdot 3\text{NH}_4\text{F}$  is obtained as a crystalline violet precipitate, slightly soluble in water, but insoluble in a solution of ammonium fluoride. If this precipitate is washed successively with water, a concentrated solution of ammonium fluoride, and strong alcohol, and exposed to the air, its violet colour changes to dirty yellow, and when perfectly dry, it has a deep yellow colour. This yellow substance dissolves completely in water, but the solution decomposes even at the ordinary temperature with evolution of bubbles of gas. When the aqueous solution is evaporated in a vacuum or by exposure to air, small brilliant transparent yellow regular octohedrons are obtained, often mixed with very slender yellow needles. If, however, the aqueous solution is mixed with ammonium fluoride, a precipitate is obtained which consists of the regular octohedrons alone. These crystals are insoluble in a solution of ammonium fluoride, but dissolve readily in water, forming a golden-yellow solution, which, when acidified with dilute sulphuric acid, bleaches, and is bleached by a solution of potassium permanganate, with evolution of oxygen. Ammonia produces a yellow flocculent precipitate, soluble in cold dilute sulphuric acid with formation of a reddish-yellow solution, which behaves in a similar manner with a solution of potassium permanganate. If the reddish-yellow solution is mixed with potassium hydrofluoride, a portion of the titanium is precipitated as  $\text{TiF}_4 \cdot 2\text{KF} + \text{H}_2\text{O}$ , and the liquid is decolorised and gives Barreswil's reaction. The octohedral crystals have the composition  $\text{TiO}_2\text{F}_2 \cdot 3\text{NH}_4\text{F}$ , and it would appear that the oxygen is in a condition similar to that in which it exists in hydrogen peroxide. This compound is the first example of a substance passing from a lower form to the highest form, in presence of the most stable or normal compound. As prepared by exposure to air, the yellow substance contains a considerable proportion of normal fluotitanate, and it is probably formed in accordance with the equation  $2(\text{TiF}_3 \cdot 3\text{NH}_4\text{F}) + \text{O}_2 = \text{TiF}_4 \cdot 3\text{NH}_4\text{F} + \text{TiO}_2\text{F}_2 \cdot 3\text{NH}_4\text{F}$ , the violet compound absorbing oxygen and splitting up into the normal salt and the oxysalt.

When hydrogen peroxide is added to a sulphuric acid solution of titanic acid in the proportion  $\text{TiO}_2 : \text{H}_2\text{O}_2$ , a reddish-yellow liquid is obtained, which gives Barreswil's reaction on adding a further small quantity of hydrogen peroxide. If the liquid is now neutralised with ammonia, a yellow solution is obtained, from which neutral ammonium fluoride precipitates yellow octohedra identical with those obtained by the other method. If sufficient ammonium fluoride is not present, the liquid remains slightly coloured, and when evaporated in presence of air, it deposits very slender yellow needles similar to those obtained by the first method. These needles consist of a hydrated oxyfluoride containing less fluorine than the octohedral compound.

This series of oxyfluorides throws light on the nature of the reac-

tion between titanitic acid and hydrogen peroxide. They are evidently derived from the radicle of the acid formed by  $\text{TiO}_3$ , in which an atom of oxygen has been replaced by two atoms of fluorine, as in the case of the oxyfluomolybdates and the oxyfluotungstates. They differ in constitution from the latter, however, in that they correspond with a higher state of oxidation. The octohedral salt is decolorised by hydrofluoric acid, the oxygen being replaced by fluorine atom for atom, that is to say, the couple  $\text{O}_2$  is equivalent to two atoms of fluorine:  $\text{TiO}_2\text{F}_2 + 2\text{HF} = \text{TiF}_4 + \text{H}_2\text{O}_2$ . In crystalline form, the compound  $\text{TiO}_2\text{F}_2 \cdot 3\text{NH}_4\text{F}$  is analogous to  $\text{NbOF}_3 \cdot 3\text{NH}_4\text{F}$ , which contains the same number of atoms.

C. H. B.

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## Mineralogical Chemistry.

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**Dopplerite.** By A. MAYER (*Landw. Versuchs.-Stat.*, **29**, 313—315).—The sample of dopplerite was obtained from peat beds in Holland: it contained 84·6 per cent. water, and in the dried substance was found 4·2 per cent. ash. The relation of carbon, hydrogen, and oxygen in the remainder led to the empirical formula  $C_{17}H_{18}O_3$ . The ash constituents were chiefly calcium carbonate and ferric oxide. Dopplerite is perfectly soluble in caustic potash or soda, but only partially in ammonia. Acids precipitate it from solution, and salts of alkaline earths throw it down in combination with base. A calcium salt was thus obtained having 8·1 per cent. of lime. J. K. C.

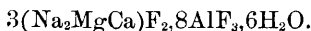
**Natural Fluorine Compounds.** By P. GROTH (*Jahrb. f. Min.*, 1883, **2**, Ref., 324—327).—This paper gives a detailed description of the fluorine minerals, analyses of which have already been published by Brandl (Abstr., 1882, 1176).

1. *Cryolite* is monoclinic:  $a : b : c = 0·9662 : 1 : 1·3882$ ,  $\beta = 89^\circ 40'$ . The planes occurring most frequently are  $\infty P$ ,  $0P$ , +  $P\infty$ ,  $R\infty$ . The chemical formula calculated from Brandl's analyses is  $3NaF, AlF_3$ .

*Pachnolite* is monoclinic:  $a : b : c = 1·1626 : 1 : 1·5320$ ,  $\beta = 89^\circ 40'$ .  $\infty P$ ,  $-P$ ,  $0P$  are the planes occurring most frequently. The rhombic section is very characteristic of pachnolite, that of thomsenolite being rectangular. The chemical formula is  $NaF, CaF_2, AlF_3$ .

*Thomsenolite* is monoclinic:  $a : b : c = 0·9959 : 1 : 1·0887$ ,  $\beta = 87^\circ 37\frac{1}{2}'$ . The most important forms are  $\infty P$ , +  $P$ ,  $0P$ . The chemical formula is  $NaF, CaF_2, AlF_3, H_2O$ .

*Ralstonite* crystallises in octohedrons. The formula is



*Chiolite* has the formula  $5NaF, 3AlF_3$ .

*Arksutite* is probably a partially altered cryolite, that is a mixture of cryolite and pachnolite. *Hagemannite* is probably thomsenolite mixed with siliceous brown ironstone. *Gearksutite* appears to be the

final product of the alteration of cryolite, whereby Na is replaced by Ca and water taken up.

2. *Fluellite* is rhombic:  $a:b:c = 0.77:1:1.874$ . Forms observed are P and 0P. Sp. gr. = 2.17. The formula is  $AlF_3 + H_2O$ .

3. *Prosopite* is monoclinic:  $a:b:c = 1.318:1:0.5912$ ,  $\beta = 86^\circ 2'$ . Forms observed are  $\infty P$ ,  $\infty P\infty$ ,  $+P$ ,  $2P2$ ,  $P\infty$ ,  $-3P\frac{1}{2}$ ,  $\infty P2$ . The formula is  $CaAl_2(FHO)_3$ .  
B. H. B.

**Zinc Blende and Prehnite from Cornwall, Lebanon Co., Pa.** By F. A. GENTH (*Jahrb. f. Min.*, 1883, 2, Ref., 322—323).—In cavities of the magnetite from Cornwall Ore Bank, fine crystals of zinc blende occur associated with prehnite, magnetite, iron pyrites, and chlorite. They have a sp. gr. of 4.033, and gave on analysis:—

S.	Zn.	Co.	Fe.	Total.
32.69	66.47	0.34	0.38	99.88

Prehnite forms crystalline incrustations upon magnetite. It has a sp. gr. of 3.042, and gave on analysis:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	H <sub>2</sub> O.	Total.
42.40	20.88	5.54	27.02	4.61	99.85

B. H. B.

**Artificial Alisonite.** By F. A. GENTH (*Jahrb. f. Min.*, 1883, 2, Ref., 324).—At the smelting works at Argo, Colorado, octohedral crystals have been observed in the furnace bottoms. They have an iron-black colour, metallic lustre, sp. gr. = 5.545, and gave on analysis the following results:—

S.	Ag.	Cu.	Pb.	Fe	Total.
15.23	2.16	51.33	31.15	trace	99.87

B. H. B.

**Rezbanyite, a New Mineral Species.** By A. FRENZEL (*Jahrb. f. Min.*, 1883, 2, Ref., 314).—This mineral occurs at Rezbanya, associated with cosalite. It has a metallic lustre, a lead-grey colour and black streak.  $H. = 2.5$  to  $3$ . Sp. gr. =  $6.09$  to  $6.38$ . It forms compact masses with copper pyrites and calcite, or is disseminated through quartz. From the analyses, the formula of rezbanyite is calculated to be  $4PbS, 5Bi_2S_3$ .  
B. H. B.

**Alloclasite.** By A. FRENZEL (*Jahrb. f. Min.*, 1883, 2, Ref., 314—315).—In order to determine the composition of this mineral, which still remains doubtful, the author made six analyses of compact material, and although the results obtained were rather variable, he is of opinion that Groth's formula  $(CoFe)(AsBi)S$ , is the correct one for this mineral.  
B. H. B.

**Kupfernickel from Colorado.** By F. A. GENTH (*Jahrb. f. Min.*, 1883, 2, Ref., 324).—In Silver Cliff, Colorado, rounded masses of kupfernickel occur in granular limestone. Sp. gr. =  $7.314$ . The analysis gave:—

As.	Sb.	S.	Cu.	Ni.	Co.	Fe.	Total.
46·81	2·24	2·52	1·59	44·76	1·70	0·60	100·22
B. H. B.							

**Corundum.** By F. A. GENTH (*Jahrb. f. Min.*, 1883, **2**, Ref., 316—319).—This paper is a description of a few remarkable occurrences, as a continuation of the paper formerly published by the author (this Jour., 1874, 549).

1. *Corundum altered into spinel* is found at the Carter Mine, Madison Co., N.C. It has a sp. gr. of 3·751. The spinel finally passes into chlorite.

The analysis, after deducting silica and corundum, gave the following results:—

Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CuO.	NiO.	ZnO.	FeO.	MgO.	Total.
66·74	1·34	0·09	0·33	0·22	11·94	19·34	100·00

Corundum altered to a slight extent into spinel has also been found at Shimersville in Lehigh Co. Sp. gr. = 4·056. After deducting 1·47 per cent. SiO<sub>2</sub>, the analysis gave:—

Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	TiO <sub>2</sub> .	Total.
56·42	13·17	22·95	4·94	2·62	100·10

2. *Corundum altered into zoisite* is of rare occurrence.

3. *Corundum altered into felspar and damourite* occurs at Unionsville. The analysis gave:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Ignition.	Total.
62·62	22·59	0·22	0·18	1·94	7·41	2·52	2·45	99·93

Another interesting occurrence is that at the Black Horse Tavern, near Media in Delaware Co. Sp. gr. = 2·611. The analysis gave:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	CaO.	BaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Ignition.	Total.
58·42	23·14	0·18	0·35	3·13	2·56	3·68	7·06	1·54	100·06

The Presley Mine in Haywood Co., N.C., has furnished some remarkable specimens of corundum altered into albite and muscovite. Analyses of the albite (I) and of the muscovite (II) are given:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Ignition.	Total.
I.	65·52	22·25	trace	—	1·96	9·54	0·53	0·22	100·02
II.	45·26	36·33	1·96	0·14	0·35	0·48	11·09	4·50	100·11

Corundum altered chiefly into damourite has been found at Belt's Bridge, Iredell Co., N.C. After deducting 3·51 per cent. of corundum, the analysis of the mica gave:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	Li <sub>2</sub> O.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Ignition.	Total.
45·96	38·22	0·61	0·37	trace	0·74	9·21	4·89	100·00

From the same locality a fragment of a hexagonal prism was found. It consisted of a core of grey corundum surrounded by mica enclosing

tourmaline, and disseminated through the unaltered tourmaline are rounded masses of garnet. The analysis of the mica gave:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	Li <sub>2</sub> O.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Ignition.	Total.
44·03	40·16	trace	3·14	trace	1·42	6·66	5·04	100·45

4. *Corundum altered into Margarite*.—This change is far less common than that into potassium mica. Remarkable specimens occur at Hendrick's Farm, Iredell Co. The analysis of the purest margarite obtainable gave:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	CaO.	Li <sub>2</sub> O.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Ignition.	Total.
32·55	48·87	0·60	0·23	10·48	trace	2·38	0·43	4·34	99·88

5. *Corundum altered into fibrolite* is found at Norwich, Conn., and at Shoup's Ford, Burke Co., N.C.

6. *Corundum altered into cyanite* is found at Statesville, Iredell Co., and in Wilkes Co., N.C.

The author comes finally to the conclusion that since the great gravel deposits in the S. States of N. America were formed, no alteration of the corundum in these deposits has taken place.

B. H. B.

**Gahnite.** By F. A. GENTH (*Jahrb. f. Min.*, 1883, 2, Ref., 321—322).—In the Deake Mica Mine, Mitchell Co., N.C., a mineral occurs which the author recognised as gahnite. It is apparently without form, has a splintery to conchoidal fracture and a dark green colour.  $H. = 7·5$ . Sp. gr. = 4·576. It gave on analysis the following results:—

Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CuO.	ZnO.	MgO.	Total.
54·86	4·50	1·14	0·29	0·30	38·05	0·79	99·93

Gahnite has also been found at the Cotopaxi Mine, Chaffee Co., Colorado. Carefully selected material gave on analysis the following results:—

Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	ZnO.	MgO.	Total.
60·76	0·58	4·56	23·77	10·33	100·00

The gahnite from Cotopaxi is frequently coated with a white earthy mineral, soluble in strong boiling hydrochloric acid. It gave on analysis the following results:—

Ignition.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CuO.	PbO.	ZnO.	MgO.	Total.
13·82	28·08	18·20	4·32	0·82	1·80	1·75	29·85	98·64

Lead and zinc are probably present as carbonates, the Fe<sub>2</sub>O<sub>3</sub> as such, and if these impurities be deducted, the composition places the mineral near ripidolite.

Another alteration of the gahnite is that into a micaceous chloritic mineral, which gave on analysis:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CuO.	ZnO.	MgO.	Ignition.	Total.
31·15	13·12	10·74	0·77	0·39	29·23	11·78	97·18

B. H. B.

**Apatite from Horrsjöberg, Sweden.** By IGELSTRÖM (*Jahrb. f. Min.*, 1883, 2, Ref., 312—313).—Apatite occurs at Horrsjöberg, together with disthene, lazulite, rutile, menaccanite, damourite, talc, triplite, and quartz, in beds conformable to the surrounding gneiss. The analysis gave:—

P <sub>2</sub> O <sub>5</sub> .	Ca.	FeO.	MnO.	
41.14	50.56	trace		B. H. B.

**Turquoise Found at Alexandria.** By A. FRENZEL (*Jahrb. f. Min.*, 1883, 2, Ref., 315).—The analysis of a turquoise found at Alexandria gave the following results:—

P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CuO.	H <sub>2</sub> O.	Organic matter.	Total.
28.14	0.68	41.09	1.08	4.54	20.96	4.49	100.98

It had a dark-green colour. H. = 5; sp. gr. = 2.39. It probably was brought to Alexandria from Sinai. B. H. B.

**Roemerite, Botryogen, and Native Magnesium Iron Sulphate.** By J. BLAAS (*Monatsh. Chem.*, 4, 833—849).—Berzelius, in 1815, described as “red iron vitriol” a mineral which was afterwards more exactly investigated by Haidinger, from whose analysis it appeared to be a hydrated sulphate of iron and magnesium. The crystals were found to be monoclinic, and from their tendency to aggregate in spherical groups, attached like bunches of grapes, the mineral received the name of *botryogen*.

Grailich, in 1858, described a new mineral, *roemerite*, which, from an analysis by Tschermak, appeared to be a hydrated sulphate of iron and zinc, and from a crystallographic examination by Grailich himself was inferred to be monoclinic, and closely related to botryogen. More recently a mineral having the characters of roemerite, but in better defined crystals, has been obtained from Persia, and examined by the author, who has shown that it has the chemical composition of roemerite, and that the crystals belong, not to the monoclinic, but to the triclinic system, exhibiting the axial ratio  $a : b : c = 0.8791 : 1 : 0.8475$ , and the axial angles  $bc = 89^\circ 44'$ ;  $ac = 102^\circ 17'$ ;  $ab = 85^\circ 18'$ . The paper gives elaborate details of the crystallographic and optical characters of the mineral.

The differences between roemerite and botryogen may be tabulated as follows:—

	Roemerite.	Botryogen.
Crystalline form . . . . .	Triclinic	Monoclinic
Habit . . . . .	Tabular	Short prismatic
Colour . . . . .	Light to dark-brown violet	Hyacinth-red to yellow
Dichroïsm . . . . .	Weak	Very decided

The author has also examined another mineral from Fahlun in Sweden, hitherto regarded as botryogen. It forms stalactites or crusts, orange-coloured on the surface, white beneath, the orange

colour disappearing when the mineral is moistened and kept for some time in a closed vessel. On closer examination, the mineral is seen to be formed of several portions, partly superposed, partly intergrown, the lowest layer consisting of a green crystalline mass resembling ferrous sulphate, but much lighter in colour, and having here and there a radiate structure. Above this is a layer composed chiefly of small splinters of magnesium sulphate imbedded in a yellowish-white fibrous mass. Chemical examination showed the presence of magnesia in the substratum consisting chiefly of ferrous sulphate, and, on the other hand, the crystals of magnesium sulphate were found to contain ferrous oxide.

An analysis of these crystals separated from the whitish-green substratum gave 31.57 per cent.  $\text{SO}_3$ , 7.25  $\text{FeO}$ , 9.05  $\text{MgO}$ , 1.64  $\text{Al}_2\text{O}_3$ , and (by difference) 50.49 water.

The compound  $\text{Fe}_2\text{SO}_4 + 7\text{H}_2\text{O}$  is known to be dimorphous, crystallising in the monoclinic system as *melanterite*, and in the rhombic as *tauriscite*, while  $\text{MgSO}_4 + 7\text{H}_2\text{O}$  is likewise dimorphous, separating in monoclinic crystals, like those of melanterite, at temperatures between  $25^\circ$  and  $30^\circ$ . It is therefore not surprising that these two members of the isomorphous group  $\text{R}''\text{SO}_4 + 7\text{H}_2\text{O}$  should occur together in nature, as well as when artificially crystallised.

H. W.

**Rutile and Zircon from the Itacolumite of Edge Hill.** By F. A. GENTH (*Jahrb. f. Min.*, 1883, 2, Ref., 322).—The itacolumite rocks of the Potsdam sandstone of Edge Hill, Bucks Co. Pa, contain exceedingly minute yellow grains consisting of rutile. Associated with the yellow grains are small crystals of tourmaline, menaccanite, and colourless or brownish-white zircons, showing the planes  $\infty\text{P}$ ,  $\text{P}$ ,  $\infty\text{P}\infty$ ,  $3\text{P}3$ .

B. H. B.

**Chemico-mineralogical Studies on Italian Minerals.** By A. FUNARO and L. BUSATTI (*Gazzetta*, 13, 433—436).—1. *Wollastonite from Sardinia*.—This mineral is found at S. Vito, a mineralogical district of Sarrabus in Sardinia, implanted on certain schists in small needles grouped in stars or rosettes. Colour light-grey. Transparent or translucent. Lustre strong and nacreous, especially along the cleavage-planes. Powder white. Hardness, 4.5. Density, 2.7 to 2.8. Heated before the blowpipe in small splinters, it melts with great difficulty, and only along the edges, to a tumefied transparent glass. Gently heated with strong hydrochloric acid it dissolves and gelatinises. Its analysis gives: 49.78  $\text{SiO}_2$ , 45.12  $\text{CaO}$ , 1.20  $\text{MgO}$ , 2.20  $\text{Fe}_2\text{O}_3$ , 0.6  $\text{H}_2\text{O}$  = 98.90, whence, regarding the greater part of the water as combined with the ferric oxide, and the excess as an impurity, varying in specimens of the mineral from different localities, we find, reducing the numbers to 100 parts: 51.80  $\text{SiO}_2$ , 46.95  $\text{CaO}$ , and 1.25  $\text{MgO}$ ; and hence, calculating the magnesia together with the lime, we deduce the formula  $\text{SiCaO}_3$ .

The rock on which this wollastonite is implanted is dark-coloured, almost black, compact, tenacious, and possesses considerable hardness. It is composed of silica, alumina, and graphite, with mere traces of earthy-alkaline metals, perhaps due to wollastonite penetrating its

mass, and not separable by mechanical means. When examined with the microscope in very thin sections, it appears to be composed of granulo-crystalline silica diffused through a petro-siliceous ground-mass or magma, exhibiting scattered reddish spots referable to limonite, and numerous black, opaque, irregularly disseminated masses, apparently consisting of graphite, and so abundant in certain sections as to render the specimen perfectly opaque. In this rock, the wollastonite appears in small crystalline masses recognisable by its fibrous structure, absence of colour, and the tints which it exhibits in polarised light.

2. *Chlorite from the Bottino (Serravezza).*—The chlorite of this mineralogical district in the Apuan Alps occurs massive and in radiate groupings, amongst the beautiful crystallisations of metallic sulphides in the quartzoso-metalliferous vein of the said district.

Aspect scaly; colour apple-green. Lustrous and minutely crystalline. The powder appears under the microscope to consist of minute greenish scales or crystalline laminae joined together in a spiral column. The crystalline laminae, usually of rounded outline, often exhibit the form of regular hexagons. When very thin, they are perfectly transparent, slightly dichroic, and exhibit faint interference colours. Hardness about 1·5. Density 2·8 to 2·9. With borax the mineral forms a bead, reddish-yellow while hot, changing as it cools to light green, and finally to yellow. Heated in a closed tube, it gives off water, turns brown, and retains that colour if heated to redness on platinum foil. Strong hydrochloric acid attacks it, eliminating at first a small quantity of carbonic anhydride, and on prolonged ebullition decomposes it completely, with deposition of gelatinous silica.

Quantitative analysis of several specimens showed the absence of alkaline bases and the presence of traces of lime in a few specimens only. The chief constituents are iron in the ferrous state, alumina, silica, and magnesia. By quantitative analysis of a specimen free from lime, Funaro obtained the results given on the first line of the following table, those on the second and third lines having been obtained respectively by Erlenmeyer and Nies (Rammelberg's *Handbuch der Mineralogie*, i, 495).

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	CaO.	H <sub>2</sub> O.	CO <sub>2</sub> .
23·69	21·63	34·33	4·27	4·82	—	7·00	4·12 = 100·06
25·72	20·69	27·79	4·01	11·70	—	10·05	— = 99·96
23·67	24·26	29·41	8·17	1·75	1·28	8·83	1·01 = 98·38

Achiardi in his *Mineralogia della Toscana* (ii, 231) mentions this chlorite, which, with reference to its external characters, he regards as a *ripidolite*, and especially as belonging to the variety called *aphrosiderite*. This conclusion is in accordance with the analyses above given. The constant presence of carbonic acid in this aphrosiderite leads to the idea that its normal composition has undergone some alteration, inasmuch as the carbonic acid must be regarded as combined with the ferrous oxide or the magnesia, and not as entering into the chloritic molecule.

H. W.

**Mineralogical Notices.** By G. FREDA (*Gazzetta*, 13, 498—499).

—1. *Green Humites from Monte Somma*.—Large crystalline grains having a light green colour and vitreous lustre. H. 6·5. Sp. gr. 3·21. Infusible before the blowpipe; loses 1·08 per cent. when strongly heated. II. *Cupriferous Variety of Pyroxene*.—Irregular kidney-shaped lumps of various sizes, having a fine sky-blue colour, and very fine granular texture. H. 5·5. Sp. gr. 3·19. Melts before the blowpipe to a glass having the colour of turquoise; its powder, which has an ashv colour, assumes a fine roseate tint when heated in the air. III. With some specimens of the last-described substance, there occurs a colourless highly translucent mineral, having a dull glassy lustre: hardness a little less than that of fluorspar, and sp. gr. = 3·05; it melts before the blowpipe to a limpid glass. IV. *New Case of Metamorphism of Leucite*.—In certain crystalline masses from Somma there occur, in the midst of a mixture of melilite, magnesia-mica, and pleonast, large scattered nodules of leucite, presenting the singular character of being formed of a white opaque zone enclosing a yellow glassy nucleus of undecomposed leucite.

The following are analyses of these minerals:—IV *a* is the white zone; *b* the same deprived of calcium carbonate; *c* the leucite nucleus.

	I.	II.	III.	IV.		
				<i>a.</i>	<i>b.</i>	<i>c.</i>
SiO <sub>2</sub> .....	35·17	52·73	46·70	38·40	42·61	55·78
F .....	3·41	—	—	—	—	—
CO <sub>2</sub> .....	—	—	—	4·27	—	—
Al <sub>2</sub> O <sub>3</sub> .....	—	1·06	1·09	20·18	20·96	22·12
Fe <sub>2</sub> O <sub>3</sub> .....	—	—	—	trace	trace	0·59
CaO .....	1·69	24·18	39·62	26·83	24·47	—
MgO .....	54·83	17·80	13·38	3·96	4·28	—
FeO .....	3·76	4·22	—	—	—	—
CuO .....	—	0·94	—	—	—	—
K <sub>2</sub> O .....	—	—	—	5·60	6·49	19·81
	98·86	100·93	100·79	99·24	98·81	98·30

H. W.

**Alteration of Talc into Anthophyllite.** By F. A. GENTH (*Jahrb. f. Min.*, 1883, 2, Ref., 320—321).—In Pennsylvania unaltered olivine rock has never yet been found. An enstatite rock has, however, been found containing small grains of olivine. It is best developed at Castle Rock, Delaware Co., and near Wood's chrome mine, Lancaster Co. Grains of chromite are disseminated throughout all the olivine rock, and throughout the serpentine which has resulted from the alteration of this rock. This is also the case with a talc which occurs near Castle Rock. This talc has a sp. gr. of 2·789 and H. = 2. The analysis gave:—

SiO <sub>2</sub> .	Chromite.	Cr <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	NiO.	FeO.	MgO.	H <sub>2</sub> O.	Total.
62·48	0·20	0·13	0·59	0·16	4·95	27·60	4·81	100·92



It is now converted into anthophyllite, for it is enveloped by a radiated fibrous mineral, which encloses, like the original talc, grains of chromite. Its sp. gr. is 2.983. The analysis gave—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	NiO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
56.88	2.45	trace	9.20	0.28	0.17	28.50	0.18	0.03	2.28	99.97

This analysis corresponds with that of the anthophyllite from Hermannschlag.  
B. H. B.

**Talc, Pseudomorphous after Magnetite.** By F. A. GENTH (*Jahrb. f. Min.*, 1883, 2, Ref., 321).—Near Dublin, in Harford Co., Md., a coarse scaly chlorite, in immediate contact with talc slate, has disseminated through it numerous small octohedrons of talc pseudomorphous after magnetite, an alteration which has never been observed before. In these crystals, the talc scales are arranged parallel to the octohedral planes, whilst in the centre there is occasionally a small nucleus of magnetite, sometimes associated with pulverulent limonite.  
B. H. B.

**Pyrophyllite in Anthracite.** By F. A. GENTH (*Jahrb. f. Min.*, 1883, 2, Ref., 323).—Pyrophyllite has recently been found near Drifton, Luzerne Co., Pa. It is found in the stratification planes and fissures, and also in the most compact anthracite. Sp. gr. = 2.81.

The analysis of a specimen from Cross Creek Colliery, near Drifton, gave:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.	Total.
65.77	29.36	0.12	4.85	100.10

B. H. B.

**Occurrence of Kaolin in North Sweden.** By A. LINDSTRÖM (*Jahrb. f. Min.*, 1883, 2, Ref., 365—366).—From the sketch map given by the author it may be seen that all the localities at which kaolin is found are situated in a zone 11—16 km. broad, and 48—54 km. long, where iron gneiss forms the adjacent rock.  
B. H. B.

**Alteration of Orthoclase into Albite.** By F. A. GENTH (*Jahrb. f. Min.*, 1883, 2, Ref., 320).—In the gneiss of Upper Avondale, Delaware Co., Pa., druses have been found lined with crystals of albite, muscovite, and sometimes with beryl, tourmaline, and calcite. The colourless albite crystals form a coating either directly above flesh-coloured orthoclase or, sometimes, with the intermediate development of greyish-white plagioclase. Analyses of the albite (I) and the flesh-coloured orthoclase (II) are given. In some instances there is, between the orthoclase and albite, a greyish felspar, which proves on analysis (III) to be a mixture of albite and oligoclase, the oxygen ratio being 1 : 3.1 : 10.6. At the same locality orthoclase has also been found in colourless crystals (Analysis IV) and in a white cleavage mass (Analysis V).

	I.	II.	III.	IV.	V.
SiO <sub>2</sub> .....	68.52	64.53	65.22	65.84	65.03
Al <sub>2</sub> O <sub>3</sub> .....	19.44	19.64	21.44	19.50	19.22
Fe <sub>2</sub> O <sub>3</sub> .....	—	trace	0.20	—	—
MnO .....	—	—	trace	—	trace
MgO .....	—	0.25	—	—	—
CaO .....	—	0.16	2.07	trace	0.32
BaO .....	—	—	—	0.08	—
Na <sub>2</sub> O .....	11.42	1.77	9.36	3.93	1.71
K <sub>2</sub> O .....	0.65	13.62	1.16	10.69	14.18
P <sub>2</sub> O <sub>5</sub> .....	—	—	—	—	0.08
Ignition .....	—	0.71	0.58	0.22	0.13
Total .....	100.03	100.68	100.03	100.26	100.67
Sp. gr. ....	2.604	2.555	2.620	2.595	2.572

B. H. B.

**Beryl and Allanite from Alexander Co., N.C.** By F. A. GENTH (*Jahrb. f. Min.*, 1883, 2, Ref., 322).—The analysis of a beryl, with a sp. gr. of 2.703, gave the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Be <sub>2</sub> O <sub>3</sub> .	FeO.	H <sub>2</sub> O.	Total.
66.82	18.60	13.61	0.22	0.83	100.08

An analysis of allanite, with sp. gr. = 3.005, from the same locality, gave:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	(CeDiLa) <sub>2</sub> O <sub>3</sub> .	Y <sub>2</sub> O <sub>3</sub> .	MgO.	CaO.
32.05	22.93	11.04	1.99	14.81	0.85	1.28	9.43
	Na <sub>2</sub> O.	K <sub>2</sub> O.	Ignition.	Total.			
	0.54	0.20	3.64	98.76			

B. H. B.

**Occurrence of Gedrite as Essential Constituent of certain Rocks.** By H. SJÖGREN (*Jahrb. f. Min.*, 1883, 2, Ref., 366—367).—Gedrite, a rhombic anthophyllite rich in alumina, occurs as essential constituent of several Scandinavian rocks. An analysis of this mineral from Hilsen gave the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	Ignition.	Total.
43.92	11.34	16.81	1.47	3.02	19.14	1.68	97.38

The alkalis were not determined.

An amphibolite schist from Hilsen, near Snarum, was found on examination to be composed half of gedrite and half of black hornblende; biotite, apatite, rutile, and magnetic pyrites occurring as accessory constituents.

B. H. B.

**The Phyllites of the Tyrolean Alps.** By A. PICHLER (*Jahrb. f. Min.*, 1883, 2, Ref., 366). This paper gives the results of the microscopic investigation of the numerous varieties of phyllite (clay-slate) which are found in the Tyrolean Central Alps. Microscopic tourma-

line occurs to a great extent, and is very characteristic. An appearance similar to the fluxion structure may frequently be detected.

B. H. B.

**Hornblende-diabase from Gräveneck.** By A. STRENG (*Jahrb. f. Min.*, 1883, 2, Ref., 367—369).—This diabase, interesting on account of the large amount of basaltic hornblende it contains, occurs at Gräveneck near Weilburg on the Lahn.

The rock is of a blue to greenish-grey colour. The analysis of the diabase disseminated through it gave the following results:—

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
44.13	2.66	7.45	7.73	7.02	20.46	10.64	0.90	1.00	101.99

Crystals of basaltic hornblende occur more rarely. The analysis of pure material, with sp. gr. = 3.25, gave:—

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.
41.35	4.97	13.48	5.14	10.33	10.93	11.44	0.62
		Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.			
		2.10	0.48	100.84			

Among the other minerals disseminated through the mass, plagioclase, iron-ore, pyrites and apatite may be mentioned. The iron ore is strongly magnetic, and contains 17.81 per cent. of TiO<sub>2</sub>. In conclusion, Senfter's complete analysis of this rock is given (this Journal, 1873, 738).

B. H. B.

**Diabase rich in Apatite from Gräveneck.** By A. STRENG (*Jahrb. f. Min.*, 1883, 2, Ref., 369—370).—This diabase occurs at Gräveneck. It contains an unusual amount of apatite columns with the forms  $\infty$ P, P, OP,  $\infty$ P<sup>2</sup>. The composition of the rock is in other respects quite normal. The analyses gave the following results:—

TiO <sub>2</sub> .	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	K <sub>2</sub> O.
2.08	46.53	18.07	6.13	7.77	0.30	7.87	3.78	0.55
		Na <sub>2</sub> O.	H <sub>2</sub> O.	CO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub>	Total.		
		3.51	2.17	0.51	1.33	100.60		

B. H. B.

**Nepheline Rocks from the Vogelsberg.** By H. SOMMERLAD (*Jahrb. f. Min.*, 1883, 2, Ref., 372).—With the nephelinite of Meiches, a basalt occurs in which Ludwig found the nephelinite in the form of veins 1.5 mm. thick. This proved to be a nepheline-basalt (Analysis I) with sp. gr. = 3.103. The nepheline-dolerite of Gunzenau occurs in blocks. The microscopic examination of the rock showed it to have the normal composition of a nepheline-tephrite, with dark mica and some olivine as accessory constituents. Sp. gr. = 2.745. The analysis gave the results given under II. The phonolites shown on the geological map of the Grand Duchy of Hesse, near Salzhausen and Herchenhain, appear to be trachytoid phonolites poor in nepheline, whilst those near Wohnfeld and Wenuigs are basalts

with a very coarsely granular structure and light colour. An analysis of the rock from Ziegenbals, near Wohnfeld, is given (III).

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.
I. ....	42·37	8·88	11·26	7·80	10·93	13·01	1·21
II. ....	49·35	11·50	6·54	9·93	5·92	3·61	2·43
III. ....	55·70	14·55	1·68	10·71	6·91	5·81	0·51

	Na <sub>2</sub> O.	H <sub>2</sub> O.	TiO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .	Total.
I. ....	4·51	0·34	1·55	0·21	102·07
II. ....	7·01	0·91	—	1·41	98·41
III. ....	4·12	0·59	0·20	0·88	101·66

B. H. B.

**Phonolites of Elfdalen.** By A. E. TÖRNEBOHM (*Jahrb. f. Min.*, 1883, 2, Ref., 370—371).—The author has discovered three veins of the so-called phonolite of Elfdalen traversing porphyry and, perhaps, also sandstone at Heden, in Dalarne. The new material allowed a more exact petrographical examination than has been the case hitherto. The ground-mass is finely granular and crystalline, and is composed of feldspar, cancrinite, nepheline, aegirine, titanite, and apatite; whilst feldspar and cancrinite occur in porphyritic crystals. The feldspar is orthoclase, microcline, and plagioclase. The cancrinite is, when fresh, colourless and perfectly clear, but alters into a brick-red and almost opaque mass, which was formerly thought to be feldspar converted into zeolite. For the rock, the author proposes the name Cancrinite-aegirine-syenite. This is not only the first time that cancrinite has been found in Sweden, but also the first time that cancrinite has been proved to be an essential constituent of a rock.

B. H. B.

**Analysis of a Meteorite which fell at Alfianello on the 13th of February, 1883.** By G. CAVAZZI (*Gazzetta*, 13, 492).—The analysis of this meteorite gave 45·1 per cent. SiO<sub>2</sub>, 3·7 S, 26·38 MgO, 19·8 Fe (as sulphide, phosphide, silicate, and metallic), perceptible traces of phosphorus, nickel, and sodium, scarcely perceptible traces of potassium, aluminium, calcium, manganese, and copper. H. W.

**Meteorite of Alfianello.** By W. FLIGHT (*Proc. Roy. Soc.*, 35, 258—260).—In this paper an analysis is given of a meteorite which fell on February 16th, 1883, at Alfianello, in the district of Verolannova, in the province of Brescia, Italy. The fall was accompanied by a loud detonation heard in the neighbouring provinces.

In structure, the meteorite belongs to the group sporadosideres oligosideres, and resembles aumalite, being nearly identical with the meteorite of New Concord, Ohio.

It was finely granular, containing disseminated metallic grains; its sp. gr. was 3·47 to 3·5.

On analysis, the following numbers were obtained:—

Troilite.....	6·919
Nickel iron .....	2·108
Soluble silicate .....	50·857
Insoluble silicate.....	40·116

The soluble silicate contained the following constituents :—

Silica.....	35·12
Ferrous oxide .....	51·43
Alumina .....	1·518
Lime .....	4·644
Magnesia .....	7·269

And the insoluble silicate had the composition—

Silica.....	56·121
Ferrous oxide .....	13·397
Chromic oxide.....	8·281
Lime .....	6·712
Magnesia .....	17·263

From the results, it appears not improbable that this latter portion contains some tridymite.

V. H. V.

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## Organic Chemistry.

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**Physical Properties of Petroleums.** By S. PAGLIANI (*Gazzetta*, 13, 495).—Mendelejeff found, for the petroleum of Baku, a very simple relation between the densities and boiling points of the several fractions, represented by the equation  $d = a + bt$ , in which  $a$  and  $b$  are constants, the values of which have to be determined by experiment for different intervals of temperature and for different kinds of petroleum in the same intervals. For the fractions of Baku petroleum boiling at 100—180°, Mendelejeff found  $d = 669.5 + 0.80t$ , and for the interval 180—240°,  $d = 712.9 + 0.56t$ , the density of water at 15° being taken as 1000. For the petroleum of Montechino near Montanaro (Piacenza), the author finds the following relations:—

$t$ ..	60—69°	90—100°	130—200°	200—250°
$d$ ..	$504.8 + 2.42t$	$593.1 + 1.68t$	$704.7 + 0.61t$	$668.2 + 0.81t$

These densities are somewhat greater than those found by Mendelejeff for the Russian petroleum. H. W.

**Dibromodinitromethane.** By S. M. LOSANITSCH (*Ber.*, 16, 2730—2731).—The author gives analytical data showing that the compound which he described as dibromodinitromethane is not a mixture of monobromodinitromethane and carbon tetrabromide, as Kachler and Spitzer (*Ber.*, 15, 471; 16, 51) assume. W. C. W.

**Conversion of Fulminates into Hydroxylamine.** By A. STEINER (*Ber.*, 16, 2419—2420).—In a former communication (*Abstr.*, 1883, 1074) the author has shown that mercury fulminate yields

hydroxylamine when treated with hydrochloric acid; a quantitative examination of this reaction shows that both the nitrogen-atoms of the fulminate are converted into hydroxylamine, lending additional support to the hypothesis that fulminic acid is an isonitroso-compound, having the formula  $\text{HO.NC:CN.OH}$ . Moreover, in mercury fulminate, the mercury can be replaced by acid radicles, by acting upon it with acetic or benzoic chlorides, and the author hopes to obtain a further clue to the constitution of fulminic acid from a study of the compounds formed.

P. P. B.

**Absorption of Ammonia-gas by Alcohols.** By S. PAGLIANI and EMO (*Gazzetta*, 13, 278).—It has been shown by one of the authors, in conjunction with Nacari, that ammonia-gas, unlike the majority of gaseous bodies, is more soluble in water than in ethyl alcohol. The present paper contains the details of similar experiments with normal propyl and isopropyl alcohols, leading to the following conclusions:—

1. Ammonia-gas is much more soluble in water than in the alcohols mentioned.

2. Ammonia-gas, within the limits of pressure observed (417 to 734 mm.), does not conform, in its absorption by these alcohols, to Henry's law, the values of  $\alpha \frac{760}{P}$  not being constant, but tending at any given temperature to diminish with increase of pressure, behaving indeed in this respect as with water.

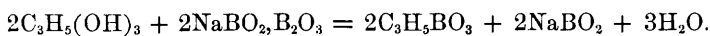
3. At equal pressure, as for all other gases, the coefficient of solubility of ammonia-gas increases with diminution of temperature.

4. At equal temperatures and pressures, the coefficient of solubility (at least for these three alcohols) diminishes as the molecular weight of the alcohol increases.

H. W.

**Action of Polyhydric Alcohols on Borax.** By W. R. DUNSTAN (*Pharm. Journ.* [3], 14, 41—44).—The author has previously shown (*Pharm. Journ.* [3], 1325) that when certain polyhydric alcohols, mannitol, erythrol, glycerol, saligenol, pyrogallol and guaiacol as well as dextrose, levulose, lactose, and mycose, are added in aqueous solution to a moderately strong solution of sodium pyroborate, they produce an acid reaction in this alkaline liquid; this acid solution becomes alkaline when largely diluted with water or when heated, in which case the liquid becomes acid again on cooling. If much more of the substance is added than is necessary to produce a distinctly acid reaction, no change is effected by heat or by dilution. These effects are not well defined when litmus is employed as an indicator, but are very distinct with phenolphthalein. Glycocine, which has many reactions in common with the above compounds, does not react in this way. In the present paper, the general reaction which gives rise to the above results is investigated. The action of glycerol on sodium pyroborate has been examined by Senier and Lowe (*Pharm. Journ.* [3], 8, 819), who concluded that boric acid, and a more basic sodium borate were formed, but were unable either directly or indirectly to isolate the free boric acid. The author shows that when anhydrous

glycerol and anhydrous sodium pyroborate are heated together at  $120^{\circ}$ , water is given off, and on extracting the mass with ether an uncrystallisable, extremely deliquescent body is obtained, which imparts a green tinge to the Bunsen flame. It was not appreciably acid in reaction, but became so on adding a small quantity of water, when a crystalline mass was formed and recognised as boric acid. This aqueous solution also contained glycerol. The original mass, after being extracted with ether, contained sodium metaborate. Thus the action of anhydrous glycerol on anhydrous sodium pyroborate yields *glycerol-borin*, ( $C_3H_5BO_3$ ), and sodium metaborate; the former compound is decomposed by water yielding boric acid and regenerating glycerol, hence the acidity which is produced when aqueous solutions of sodium pyroborate and glycerol are mixed. The above reactions are represented thus:



As water itself is a product of this decomposition, the reaction is never complete, except at high temperatures, owing to the partial conversion of the glycerol-borin into boric acid, thus:  $C_3H_5BO_3 + 3H_2O = C_3H_5(OH)_3 + H_3BO_3$ . In aqueous solution, the reaction is  $2C_3H_5(OH)_3 + (2NaBO_2 \cdot B_2O_3) + 3H_2O = 2NaBO_2 + 2H_3BO_3 + 2C_3H_5(OH)_3$ . The action of mannitol on sodium pyroborate has been studied by Klein (*Bull. Soc. Chim.*, **29**, 359), who, by precipitating aqueous solutions of these compounds with alcohol, obtained a substance which was not fully examined, but was supposed to be a conjugate acid. In a similar manner Klein obtained a barium biboromannitate. The author points out that Klein's investigation deals only with a secondary reaction, owing to the influence of the water employed in his experiments. By the action of anhydrous mannitol on anhydrous sodium pyroborate at  $140^{\circ}$ , a mass was obtained which yielded to ether a substance crystallising with difficulty in feathery tufts and giving a vivid green flame reaction. This body was easily soluble in absolute alcohol, the solution being but faintly acid, although the aqueous solution was strongly so, and gave the reaction for boric acid and for mannitol. The mass which had been extracted by ether contained sodium metaborate. These experiments indicate that mannitol decomposes sodium pyroborate in a manner similar to glycerol. The action of dextrose and levulose, when heated with anhydrous sodium pyroborate, was also examined, and in each case a substance was extracted by ether giving a green flame reaction, whilst the residue contained sodium metaborate.

The nature of the primary reaction between sodium pyroborate and glycerol, mannitol, dextrose, and levulose having been thus determined, it was found by further experiments that the change from acidity to alkalinity, occasioned by heat in aqueous solutions, was due to the dissociation of the undecomposed sodium pyroborate and metaborate. When boric acid or other acid is added to an aqueous and therefore partially decomposed solution of sodium meta- or pyroborate, until the liquid is faintly acid, alkalinity is reproduced by the addition of more water as this further decomposes these salts, liberating alkali in quantity more than sufficient to neutralise the acid.



The same result is obtained when the faintly acid liquid is heated, but the acidity is reproduced as the solution cools. W. R. D.

**Synthesis of Lecithin.** By F. HUNDESHAGEN (*J. pr. Chem.* [2], 28, 219—255).—As Diaconow has stated that lecithin splits up into neurine and disteryl glycerol phosphoric acid on treatment with dilute sulphuric acid, the first step towards the synthesis of lecithin was to prepare this acid, which can exist in two isomeric forms:  $(\text{CH}_2\text{.OSt})_2\text{CH.O.PO(OH)}_2$  or  $\text{CH}_2(\text{OSt}).\text{CH(OSt)}. \text{CH}_2\text{.O.PO(OH)}_2$ , where  $\text{St} = \text{CO.C}_{17}\text{H}_{35}$ . Two general methods seemed to be adapted for this purpose, namely, substitution of the hydroxylic hydrogen in glycerol phosphoric acid by stearyl, or the union of phosphoric acid with a glyceryl stearate. From the readiness with which glycerol phosphoric acid decomposes, experiments based on the first method did not yield the desired result, although they gave rise to some new compounds which are described further on.

Amongst the reactions founded on the second method, the action of phosphoric acid, tribasic potassium phosphate, and phosphorus oxychloride on tristearin all failed to form the distearyl acid, but better results were obtained with distearin.

*Monostearin* was prepared by heating stearic acid with anhydrous glycerol (2.5 parts) in sealed tubes at  $200\text{--}220^\circ$  for about 40 hours; and the upper layer consisting of the crude monostearin was purified by repeated crystallisation from alcohol and ether. It melts at  $60\text{--}62^\circ$ , and is very soluble in warm alcohol and ether. The *distearin* was prepared by heating molecular weights of stearic acid and crude monostearin in a retort at  $150\text{--}180^\circ$ , until the water which distilled over was that which should have been eliminated theoretically; it is advisable to somewhat increase the temperature (to  $200^\circ$ ) towards the end of the reaction. To purify the crude product, it is first heated with absolute alcohol (50—60 parts), when the greater part of the distearin remains undissolved, and nearly all the rest is deposited as the liquid cools; the monostearin and stearic acid remain in solution. The distearin is then dissolved in hot light petroleum, agitated with calcium hydroxide to remove the last traces of stearic acid, and the distearin which separates on cooling is repeatedly recrystallised from light petroleum until its melting point is constant at  $76.5^\circ$ . It crystallises from hot alcohol, in which it is but sparingly soluble (1 : 150) in tufts of glistening needles. From ether, petroleum, benzene, &c., in which it is far more soluble, it separates in compact nodules built up of slender needles.

Although there appeared to be another isomeric distearin in the mother-liquors, as well as other easily soluble compounds, the author was unable to isolate them, and therefore confined his investigations to the derivatives of the distearin just described, which he calls  $\alpha$ -distearin.

*Ammonium distearyl glycerol*,  $\text{C}_3\text{H}_5(\text{OSt})_2.\text{ONH}_4$ , is obtained as a voluminous precipitate consisting of thin prismatic crystals on passing dry ammonia into a warm ethereal solution of distearin. It is somewhat unstable, losing part of its ammonia on exposure to the air, and the whole at  $100\text{--}120^\circ$ . The corresponding sodium compound seems

to be formed on treating a benzene solution of distearin with sodium; the metal dissolves, with evolution of hydrogen, and the liquid gradually becomes changed into an opalescent gelatinous mass.

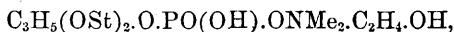
*Acetyl distearyl glycerol* is formed when distearin is heated with acetic anhydride, acetic acid, and metaphosphoric acid at  $120^{\circ}$ ; no doubt acetic anhydride alone with distearin would give the same result. After being purified by crystallisation from alcohol, it melts at  $28-30^{\circ}$ . It does not crystallise well, and decomposes when strongly heated.

*$\alpha$ -Distearylglycerolphosphoric Acid.*—This acid is formed when distearin is heated with ethylphosphoric acid, metaphosphoric acid, or phosphoric anhydride. The best method is to heat the distearin with about its own weight of phosphoric anhydride for some hours at  $100-110^{\circ}$ : the product is macerated under alcohol, digested for some time with warm alcohol to remove adhering phosphoric acid, and finally collected and washed with cold alcohol. The residue containing distearin and the glycerol acid is now extracted with hot alcohol, and excess of finely powdered sodium hydroxide is added to the hot solution, when carbonic anhydride is evolved, and the sodium salt of the acid separates; this is collected at once and washed with hot alcohol. In the washings there is, besides sodium stearate and ethyl stearate, a readily soluble sodium salt of an acid containing phosphorus, probably an isomeric distearylglycerolphosphoric acid; this crystallises in scales melting at about  $60^{\circ}$ . The crude sodium salt above mentioned is purified by repeated recrystallisation from light petroleum. The free acid may be obtained from this by dissolving it in a little warm acetic acid, decomposing it with dilute sulphuric acid, collecting the acid which is deposited in a flocculent state, and purifying it by solution in ether and evaporation. The acid is, however, more conveniently prepared from the ammonium salt obtained by passing ammonia into a warm petroleum solution of the crude acid, collecting the crystalline precipitate, and washing it with hot alcohol; when this is heated at  $130-140^{\circ}$  for some time, ammonia is given off, and the free acid is left. It crystallises from its solutions as a fatty mass consisting of minute needles, which soften at  $55^{\circ}$  and melt at  $62.5^{\circ}$ . It is easily decomposed when heated with dilute acids. The author has prepared and described the potassium, sodium, ammonium, calcium, ferrous, ferric, copper, lead, silver, and mercury salts of the  $\alpha$ -distearylglycerolphosphoric acid. Both the acid and its salts burn with a green-edged flame when strongly heated.

*$\alpha$ -Distearylglycerolphosphoric chloride* is formed when distearin (4 parts) is heated with phosphorus oxychloride (1 part); hydrochloric acid is evolved, and a very dark-brown liquid is left; this is first freed, as far as possible, from hydrochloric acid and excess of oxychloride by a current of warm air, then taken up with ether, and the ethereal solution mixed with about twice its volume of absolute alcohol, when dark-brown impurities are thrown down and are removed by filtration. The ethereal solution is evaporated in a vacuum, and the crystalline crusts which form again dissolved in a little ether and evaporated. The colourless crystals of the chloride obtained in this way are very soluble in most menstrua, melt at  $24^{\circ}$ , and are somewhat

hygroscopic. It is very readily decomposed; with water at the ordinary temperature, it yields stearic acid, glycerolphosphoric acid, and hydrochloric acid, but no distearyl-glycerolphosphoric acid.

When distearyl-glycerolphosphoric acid is warmed with a slight excess of neurine carbonate in alcoholic solution, and then evaporated, an indistinctly crystalline hygroscopic mass is left, which is easily soluble in water, alcohol, and ether. The neutral neurine distearyl-glycerolphosphate crystallises from the last-mentioned solvents in minute needles. The acid distearyl-glycerolphosphate,



is obtained by mixing neurine and the acid in proper proportions in alcoholic solution and evaporating. Its properties differ entirely from those of lecithin, so that these are isomeric compounds.

The author then gives an account of some neurine compounds. The *hydrochloride* is dimorphous, crystallising in long needles and in thin rhombic plates. The iodide of the hydrochloride,  $\text{CINMe}_2.\text{C}_2\text{H}_4.\text{I}$ , obtained by the action of strong hydriodic acid on the hydrochloride, separates from hot solutions in prisms, and from cold in rhombic plates. The iodide of the hydriodide forms thin iridescent plates. The platinochloride is trimorphous, crystallising in large orange-coloured prisms, in red-brown rhombic plates, and in regular octohedrons; both the other forms gradually change into the rhombic plates. This change can be easily seen under the microscope, and a detailed description of the best methods of observing it is given.

The platinochlorides of other two bases formed during the preparation of neurine are also described; one of these the author believes to be an amine, the other a higher homologue of neurine.

In an appendix, some substances which have been prepared in the course of this research are described.

By the action of metaphosphoric acid at  $120\text{--}150^\circ$  on distearin that was not quite pure, the sodium salt of an acid containing stearyl and phosphoric acid was obtained; it is easily soluble in water, and crystallises in needles which melt at about  $35^\circ$ . The sodium salt is insoluble in alcohol, but soluble in ether, and very soluble in water. It is possibly a monostearyl-glycerolphosphoric acid derived from monostearin existing as an impurity in the distearin.

Another sodium salt, insoluble in water, was obtained by treating ethyl phosphate with distearin in alcoholic solution, distilling off the residue, and converting the acids into sodium salts. The sodium salt is almost insoluble in water and ether, but easily soluble in aqueous alcohol, and crystallises in microscopic scales.

*Monostearyldiglycerol*,  $\text{C}_3\text{H}_5(\text{OH})(\text{OSt}).\text{O}.\text{C}_3\text{H}_5(\text{OH})_2$ , was prepared by heating stearic acid and glycerol at  $230\text{--}250^\circ$ . It is very soluble in ether and in hot alcohol, crystallising from the latter in microscopic plates which melt at about  $30^\circ$ .

*Normal glyceryl phosphate*,  $\text{C}_3\text{H}_5:\text{PO}_4$ , seems to be formed when glyceryl tribromide,  $\text{C}_3\text{H}_5\text{Br}_3$ , is treated with normal silver phosphate. A syrupy substance is obtained which, when heated with water, yields glycerolphosphoric acid. The normal phosphate seems to be decomposed in a somewhat similar manner by treatment with alcohol,

for when glyceryl tribromide is heated at  $200^{\circ}$  with silver phosphate and absolute alcohol, two isomeric *diethylglycerolphosphoric acids* are formed, apparently  $\text{CH}_2(\text{OEt})\cdot\text{CH}(\text{OEt})\cdot\text{CH}_2\cdot\text{O}\cdot\text{PO}(\text{OH})_2$  and  $(\text{CH}_2\cdot\text{OEt})_2\cdot\text{CH}\cdot\text{O}\cdot\text{PO}(\text{OH})_2$ . The contents of the tubes are filtered from silver bromide, the alcohol removed by distillation, and the syrupy residue dissolved in water and saturated with barium carbonate. On concentrating the clear solution and adding alcohol, the barium salts are precipitated; these may, to a certain extent, be separated by carefully evaporating the aqueous solution of this precipitate; the barium salt of one of the acids thus separates as a white granular precipitate, whilst the amorphous barium salt of the other acid remains in solution.

C. E. G.

**Behaviour of Dextrose with Ammoniacal Alkaline Silver Solution.** By B. TOLLENS (*Landw. Versuchs.-Stat.*, **29**, 392—395).—With silver solution containing 0.024 gram Ag to the cubic centimeter, and prepared with equal quantities of silver nitrate and caustic soda dissolved in excess of ammonia, dextrose reduces 12 atoms of silver: the reaction seems to follow the equation  $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O} = 6\text{CH}_2\text{O}_2$ , formic acid being the chief product. The author discusses the bearings of this reaction on the constitution of dextrose, and infers that it does not contain either an aldehyde or ketone group.

J. K. C.

**A New Saccharin from Milk-sugar.** By H. KILIANI (*Ber.*, **16**, 2625—2629).—By the action of lime on milk-sugar and on maltose, Cuisinier (*Monit. Scient.*, 1882, 520) obtained the lime salt of a lactone,  $\text{C}_6\text{H}_{10}\text{O}_5$ , which he named isosaccharin to distinguish it from Peligot's saccharin. In preparing large quantities of isosaccharin, the author has discovered a new saccharin (*metasaccharin*). 1 kilo. milk-sugar is dissolved in 9 litres of water, 450 grams of calcium hydrate added to the cold solution, and the whole allowed to stand for six weeks with repeated agitation; the clear brown solution is separated by a syphon, saturated with carbonic anhydride, and heated to boiling. On evaporating the filtrate to about 2 litres, an abundant separation of calcium isosaccharylolate takes place, and, after 24 hours, is filtered off and washed with cold water. After leaving a portion of the filtrate for several months in a closed bottle, a crystalline layer separated at the bottom, whilst mould formed on the surface of the liquid, and on purifying the crystals, a calcium derivative was obtained very sparingly soluble in cold water and crystallising in nodules or hard crusts consisting of microscopic prisms. It is the calcium compound of a new saccharinic acid, its formula being  $(\text{C}_6\text{H}_{11}\text{O}_6)_2\text{Ca} + 2\text{H}_2\text{O}$ ; it loses its water of crystallisation at  $120$ — $130^{\circ}$ . On decomposing its solution with oxalic acid and evaporating the filtrate, moderately large colourless rhombic crystals of *metasaccharin* are obtained, having a slightly bitter taste, and showing a perfectly neutral reaction. Its formula is  $\text{C}_6\text{H}_{10}\text{O}_5$ , but its properties are very different from those of Peligot's saccharin and Cuisinier's isosaccharin; it crystallises in the rhombic system:  $a:b:c = 0.6236:1:8.988$ . Its aqueous solution is laevorotatory  $[\alpha]_D = -48.4$ , whilst saccharin and isosaccharin are dextrorotatory. It softens at  $135^{\circ}$ , becomes completely liquid at  $142^{\circ}$ , and,

after resolidifying, melts at 141—142°. It dissolves readily in cold water, its solubility being intermediate between that of isosaccharin and of saccharin; the solution becomes acid on standing, probably through the formation of metasaccharinic acid. It is readily soluble in alcohol, very sparingly in ether. Like saccharin and isosaccharin, it yields salts of the corresponding saccharinic acid by boiling with metallic oxides or carbonates; the copper salt,  $(C_6H_{11}O_6)_2Cu + 2H_2O$ , forms greenish wart-like clusters of microscopic scales. On repeating the experiment, the author finds that calcium metasaccharin is a constant product of the action of lime on milk-sugar. A. K. M.

**Elementary Composition of Wheat-starch, and the Action of dilute Acetic Acid on Starch.** By L. SCHULZE (*J. pr. Chem.* [2], 28, 311—338).—The author has examined wheat-starch in the manner detailed by F. Salomon in his paper on potato-starch (*Abstr.*, 1882, 1183), for the purpose of satisfactorily deciding whether the formula  $C_{30}H_{62}O_{31}$ , given by Naegeli, is correct. The results point conclusively, in the author's opinion, to the formula  $C_6H_{10}O_5$ . Wheat-starch carefully washed first with dilute caustic soda, then with dilute hydrochloric acid, afterwards with water, and finally air dried, was found to consist of 79.696 per cent. pure starch, 20.143 per cent. water, 0.061 per cent. ash, and 1.1 per cent. insoluble residue. Four series of experiments were carried out. I. The conversion of the starch by hydrochloric acid (the reaction is incomplete with sulphuric acid) and estimation of the resulting dextrose by a copper salt (Allihn's method); 100 parts absolutely pure starch (or 127 parts air dried) gave 110.986 parts dextrose, whilst theory requires 111.1 parts for the formula  $C_6H_{10}O_5$ . II. The conversion by hydrochloric acid and estimation of the dextrose by the sp. gr.; the average of four determinations gave 111.4 parts dextrose per 100 parts chemically pure starch. III. The conversion by hydrochloric acid and the observation of the rotatory power of the resulting dextrose solution; the average of four determinations gave 111.85 per cent. dextrose per 100 parts pure starch. IV. The elementary analysis of the purified air-dried starch, calculated from the amount chemically pure starch contained; the average of six combustions agrees with the formula  $C_6H_{10}O_5$ .

Little being known of the action of dilute acetic acid on starch, and that little being of a contradictory nature, a number of experiments on various starches with various strengths of acid were made. The best results were obtained with rice-starch in a 10 per cent. solution with 20 per cent. acetic acid. The results show that by heating rice-starch with acetic acid for four hours under pressure, almost the whole is converted into dextrin (Bondonneau's dextrin,  $\alpha$ -modification), and only traces of dextrose are formed. By continued action of heat, however, the dextrin is slowly converted into dextrose.

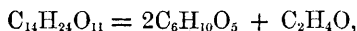
A. B.

**Inulin in the Artichoke.** By PISTONE and DE REGIBUS (*Pharm. Journ.* [3], 14, 52).—The bracts of the artichoke, *Cynura scolymus*, were boiled with water and pressed, the liquid filtered, and again boiled and filtered when hot. The solution when slowly cooled deposited a white flocculent substance which, after being washed with

boiling water and alcohol, was proved to be nearly identical with Sach's spherocrystals of inulin: it was not coloured by iodine, and was lævorotatory.

W. R. D.

**Chemical Composition of Woody Tissues.** By N. SCHUPPE (*Pharm. Journ.* [3], 14, 52).—The cellulose obtained from the woody tissues of pine, poplar, mahogany, American and European nut, oak, and alder, by treatment with nitric acid and potassium chlorate, has the same composition as pure cellulose,  $C_6H_{10}O_5$ . The wood of the European and American nut nearly coincides in composition with cellulose; that of mahogany and oak has the formula

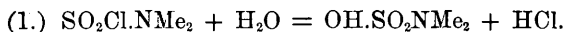


and the wood of poplar and alder the formula  $C_8H_{14}O_6 = C_6H_{10}O_5 + C_2H_4O$ . The proportion of lignin to cellulose is fairly constant in different woods, 17.6 per cent. of lignin to 40.7 per cent. of cellulose. The author considers that lignin has the formula  $C_{19}H_{18}O_8$ , which is nearly identical with that of catechin, and hence obtains as an approximate formula for woody fibre,  $5C_6H_{10}O_5 + C_{19}H_{18}O_8$ . Only a trace of gum was found in the wood of conifers, but 3.25 per cent. in poplar and 7.09 per cent. in alder.

W. R. D.

**Action of Sulphonic Chloride on Secondary Amines.** By R. BEHREND (*Annalen*, 222, 116—136).—In studying the action of sulphonic chloride on ammonia, Regnault (*J. pr. Chem.*, 18, 98) obtained sulphonamide,  $SO_2(NH_2)_2$ , but was unable to separate it from the simultaneously formed ammoniac chloride. Wenghöffer (*J. pr. Chem.*, 16, 448), in acting with sulphonic chloride on aromatic amines, obtained only chlorine-substituted amines. The author has studied the action of sulphonic chloride on secondary fatty amines, which behave very differently. The action of sulphonic chloride on dimethylamine has been already described (Abstr., 1881, 716), as also that of sulphonic chloride on the hydrochloride of dimethylamine (Abstr., 1882, 164), whereby dimethylamidodisulphonic chloride is formed. An equally good yield is obtained if crude trimethylamine is employed; it is only, however, the dimethylamine in the latter which takes part in the reaction. If a chloroform solution of dimethylamidodisulphonic chloride is added to dimethylamine, tetramethylsulphonamide is formed, which can be purified as above:— $SO_2Cl.NMe_2 + 2NHMe_2 = (NMe_2)_2SO_2 + NH_2Me_2Cl$ . Tetramethylsulphonamide is decomposed by gaseous hydrochloric acid at  $120^\circ$ , dimethylamidodisulphonic chloride and dimethylamine hydrochloride being formed:— $(NMe_2)_2SO_2 + 2HCl = SO_2Cl.NMe_2 + NH_2Me_2Cl$ . Aniline and dimethylamidodisulphonic chloride yield dimethylphenylsulphonamide,  $Me_2N.SO_2NH.Ph$ , crystallising in needles, and melting at  $84-85^\circ$ , was prepared. This body dissolves in sodium hydroxide with formation of a sodium compound,  $NMe_2.SO_2.NPhNa$ , which is decomposed by hydrochloric or carbonic acid, with reproduction of the sulphonamide. Similar compounds were prepared by employing paratoluidine instead of aniline. Dimethylamidodisulphonic chloride is only slowly acted on by cold water, but on heating it is principally

converted into dimethylsulphonamic acid, a small quantity of acid dimethylamine sulphate being formed at the same time:—



(2.)  $\text{SO}_2\text{Cl.NMe}_2 + 2\text{H}_2\text{O} = \text{OH.SO}_2\text{ONHMe}_2 + \text{HCl}$ . The ether of this acid was prepared by heating an alcoholic solution of dimethylamidodisulphonic chloride with sodium ethylate:— $\text{SO}_2\text{Cl.NMe}_2 + \text{NaOEt} = \text{NaCl} + \text{SO}_2(\text{OEt})\text{NMe}_2$ . On reducing the amidodisulphonic chloride with tin and hydrochloric acid, the following reaction takes place:— $\text{SO}_2\text{Cl.NMe}_2 + 4\text{H}_2 = \text{SH}_2 + \text{NH}_2\text{Me}_2\text{Cl} + 2\text{H}_2\text{O}$ , whilst with zinc-dust the tetramethylsulphonamide is formed:— $\text{SO}_2\text{Cl.NMe}_2 + \text{Zn} = \text{SO}_2(\text{NMe}_2)_2 + \text{ZnCl}_2 + \text{SO}_2$ . Diethylamidodisulphonic chloride was prepared in the same way as the corresponding methyl compound; it is, however, far less active than the latter. By the action of dimethylamine on diethylamidodisulphonic chloride, the same dimethyldiethylsulphonamide is formed as when diethylamine acts on dimethylamidodisulphonic chloride, as was to be anticipated from analogy with the substituted carbamides.

P. F. F.

**Trimethylamine Aurochloride.** By C. E. ZAY (*Gazzetta*, **13**, 420—421).—This salt, originally obtained, but not described, by Vincent (*Bull. Soc. Chim.* [2], **27**, 194), is easily prepared by adding a concentrated solution of auric chloride to a solution of trimethylamine hydrochloride, washing the resulting precipitate on a filter with ether, which removes only the excess of gold chloride, whereas water would dissolve some of the aurochloride itself. The dried salt forms a crystalline mass having a fine chrome-yellow colour and an odour of putrid fish. It is permanent in a vacuum, but slowly turns brown on exposure to the air. On heating it, the fishy odour becomes stronger; at 220° the salt melts, and at higher temperatures it decomposes, leaving metallic gold. The salt is anhydrous, and has the formula  $\text{NMe}_3\text{HCl.AuCl}_3$ . It dissolves readily in water and in alcohol, but is insoluble in ether. The aqueous solution, when allowed to evaporate at ordinary temperatures, leaves the salt in well-defined transparent brown-yellow crystals, likewise anhydrous.

H. W.

**Tetramethylammonium Cyanide.** By C. M. THOMPSON (*Ber.*, **16**, 2338—2345).—This compound can be obtained by adding an excess of hydrocyanic acid to a strong solution of tetramethylammonium hydroxide; the solution when evaporated yields a brown crystalline mass, which may be obtained in prisms by recrystallisation from alcohol. The cyanide may also be prepared by decomposing the double cyanide of silver and tetramethylammonium with sulphuretted hydrogen. This cyanide gives the reactions of cyanides, and is decomposed by the weakest acids, with liberation of hydrocyanic acid. It volatilises at 225—227° without melting, producing alkaline vapours having an odour of trimethylamine and carbylamine. Tetramethylammonium cyanide when saponified with caustic potash behaves like potassium cyanide, yielding ammonia, formic acid, and a tetramethylammonium compound.

*Double salt of silver cyanide with tetramethylammonium cyanide,*

$\text{NMe}_3\text{CN}, \text{AgCN}$ , is obtained by adding silver cyanide to a warm solution of tetramethylammonium iodide. It crystallises from hot alcohol in long, slender, colourless needles; is slightly deliquescent, and insoluble in ether, benzene, light petroleum, and chloroform; it melts at  $211-212^\circ$ . This salt is also formed on adding silver cyanide to a solution of tetramethylammonium cyanide. On distillation, this double salt yields a residue of silver cyanide and a distillate containing trimethylamine, carbylamine, and acetonitril; this distillate, treated with an alcoholic solution of trimethylamine and silver cyanide, yields a solid compound containing both cyanogen and silver, which could not be proved to be identical with the double cyanide of silver and tetramethylammonium. Acetonitril and trimethylamine do not appear to combine. P. P. B.

**Hexmethylenamine.** By L. PRATESI (*Gazzetta*, **13**, 437—438).—It is known that trioxymethylene,  $\text{C}_3\text{H}_6\text{O}_3$ , is easily converted by ammonia into Butlerow's hexmethylenamine,  $(\text{CH}_2)_6\text{N}_4$ , which when treated with silver nitrate gives a white crystalline precipitate, permanent or nearly so in diffused daylight when dry, decomposing with slight deflagration when heated. This precipitate, not hitherto analysed, has been found by the author to contain 18.03 per cent. carbon, 3.46 hydrogen (mean of two analyses), 19.32 nitrogen, and 40.60—40.73 silver, leading to the formula  $2\text{C}_6\text{H}_{12}\text{N}_4, 3\text{AgNO}_3$ . This compound, slightly soluble in cold water, dissolves more freely in boiling water, but with partial decomposition, producing a specular deposit of silver on the sides of the vessel. From a hot solution, it separates on cooling in needle-shaped crystals. H. W.

**Isobutylbiguanide**,  $\text{C}_6\text{H}_{15}\text{N}_5 = \text{C}_2\text{H}_6(\text{C}_4\text{H}_9)\text{N}_5$ , and its Compounds. By A. SMOLKA (*Monatsh. Chem.*, **4**, 815—832).—*Cupric Isobutylguanide Sulphate*,  $(\text{C}_6\text{H}_{14}\text{N}_5)_2\text{Cu}, \text{H}_2\text{SO}_4$ , is prepared by mixing a solution of cupric sulphate with a solution of isobutylamine (of about 20 per cent.) in such quantity as to form a dark-blue perfectly clear liquid, mixing this solution with dicyanodiamide, and either leaving the mixture to itself at the temperature of the air, or heating it in a sealed tube at about  $100^\circ$ . In the latter case, the salt separates after ten or twelve hours on the sides of the tube, as a dark-red granular film, the liquid at the same time assuming a red-violet colour. At ordinary temperatures, a lighter-coloured deposit is obtained after about a week, and the mother-liquors, if left over night in a vessel cooled by ice, deposit a small additional quantity of the compound lighter in colour than either of the preceding. The formation of this copper-compound is represented by the equation  $2\text{C}_2\text{H}_5\text{N}_4 + 2\text{C}_4\text{H}_{11}\text{N} + \text{CuSO}_4 = (\text{C}_6\text{H}_{14}\text{N}_5)_2\text{Cu}, \text{H}_2\text{SO}_4$ .

This sulphate separates from solution at temperatures above  $60^\circ$  in crimson anhydrous grains; from concentrated solutions at ordinary temperatures, in rose-red crystals with 1 mol.  $\text{H}_2\text{O}$ ; and from dilute solutions at  $0^\circ$  in light rose-coloured crystals containing  $3\text{H}_2\text{O}$ . The crystal-water is given off slowly, but completely, at  $105-110^\circ$ ; more quickly at  $125-130^\circ$ . The salt may be heated to  $140^\circ$  without decomposition.

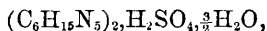


The *hydrochloride*,  $(C_6H_{14}N_5)_2Cu, 2HCl + \frac{1}{2}H_2O$ , obtained by decomposing the sulphate with barium chloride, crystallises in pale rose-red microscopic needles, often forming hemispherical or kidney-shaped groups, and like the sulphate, bears a heat of  $140^\circ$  without decomposition. 1 part of this salt dissolves in 37·76 parts water, forming a deep violet solution: the salt is insoluble in alcohol. Zinc or iron immersed in the neutral aqueous solution throws down the whole of the copper, leaving in solution the hydrochloride of isobutylbiguanide.

The *nitrate*,  $(C_6H_{14}N_5)_2Cu, 2HNO_3$ , prepared by decomposing the sulphate with barium nitrate, remains, after evaporation of its solution in a vacuum, in rose-red crusts and spherical groups, resembling those of the hydrochloride. When heated on platinum-foil, it decomposes with glimmering combustion, giving off vapours smelling of isobutylamine, and leaving cupric oxide. It is much less soluble than the hydrochloride; the aqueous solution is violet.

*Cupric Isobutylbiguanide*,  $(C_6H_{14}N_5)_2Cu$ , is best prepared by treating the hydrochloride or nitrate with soda-lye, whereupon it separates as a bulky rose-coloured precipitate, which, after draining and drying, forms a thick magma of rose-red silky needles, dissolving very sparingly in cold, somewhat more freely in hot water, with red-violet colour, and remaining on evaporation over sulphuric acid in carmine-coloured crystalline granules. It is a strong base, exhibiting great affinity for acids, including carbonic acid; its aqueous solution has an alkaline reaction, and it expels ammonia from sal-ammoniac on boiling. It dissolves readily in dilute nitric and hydrochloric acids, forming at first the corresponding salts of the copper-base, but if the acid is in excess, the copper is dissolved out and a salt of the non-cupreous base is produced.

SULPHATES OF ISOBUTYLBIGUANIDE.—The *normal sulphate*,



is prepared by triturating the corresponding salt of the copper-base with water, rinsing it into a flask, and heating it in a water-bath while a slow stream of hydrogen sulphide is passed through the liquid for several hours. On filtering from the copper sulphide, and evaporating, first on the water-bath and finally in a vacuum over sulphuric acid, the normal sulphate is obtained in large limpid crystalline laminae, and, after recrystallisation, in transparent triclinic prisms which are permanent in the air, but slowly effloresce in a vacuum over sulphuric acid, and melt and decompose when heated on platinum foil. The crystals dissolve in 3·8 parts water at  $16^\circ$ , forming a neutral solution, which is precipitated by alcohol. The *acid sulphate*,  $C_6H_{15}N_5, H_2SO_4, \frac{3}{2}H_2O$ , crystallises in large transparent plates, much more soluble than the normal salt, and is precipitated from the solution by alcohol.

HYDROCHLORIDES.—The *normal salt*,  $C_6H_{15}N_5, HCl$ , obtained by decomposing the warm solution of the normal sulphate with barium chloride, forms, after repeated crystallisation, long thin transparent brittle anhydrous prisms, soluble in 2·5 parts water at  $16\cdot5^\circ$ , melting at  $216^\circ$ , and decomposing when more strongly heated on platinum foil. The *acid salt*,  $C_6H_{15}N_5, 2HCl$ , crystallises with great difficulty

from its aqueous solution; from alcohol, it separates in anhydrous needles often grouped in feathery tufts, and is precipitated from its alcoholic solution by ether. It is deliquescent, has an acid reaction, and melts at  $194^{\circ}$ . The *platinochloride*,  $C_6H_{15}N_5, H_2PtCl_6, H_2O$ , crystallises from alcohol in fan-shaped groups of yellow four-sided plates; from water in crusts composed of yellow needles.

*Isobutylbiguanide*,  $C_6H_{15}N_5 = C_2H_5(C_4H_9)N_5$ , is obtained by decomposing the normal sulphate with the requisite quantity of baryta-water, and, after evaporation in a vacuum over sulphuric acid, forms a thick uncrystallisable syrup. Its aqueous solution has a strongly alkaline reaction, decomposes ammonium salts at a gentle heat, and when added to salts of most of the heavy metals, or to those of Al, Mg, Ca, Sr, and Ba, immediately throws down the corresponding hydroxides, especially those of the three last-named metals. It quickly absorbs carbonic acid from the air, and solidifies to a mass of deliquescent needles consisting of the carbonate.

As regards the position of the alkyl-radicle in isobutylbiguanide, it may be observed that, on heating the compound with chloroform and alcoholic soda-lye, the corresponding carbylamine or isocyanide is given off, and may be recognised by its characteristic odour; and as the formation of isocyanides is very characteristic of amines, it appears not improbable that the alkyl is situated in an amidogen-rather than in an imidogen-group.

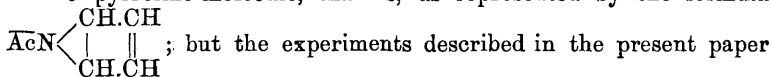
If then biguanide be represented, as in the author's paper, by the formula  $NH_2.C(NH).NH.C(NH).NH_2$ , its isobutyl-derivative must have the constitution  $NH(CH_2Pr^s).C(NH).NH.C(NH).NH_2$ , but if biguanide be correctly represented by Emich's formula



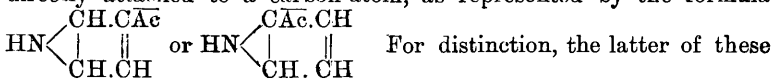
(this Journal, 1883, Abstr., 973), then isobutyl-biguanide must be constituted as shown by the formula  $NH : C(NH.CH_2Pr^s).NH.C(NH_2) : NH$ .

H. W.

**Acetyl-pyrroline and Pseudoacetyl-pyrroline.** By G. L. CIAMICIAN and M. DENNSTEDT (*Gazzetta*, 13, 455—465; and *Ber.*, 16, 2348—2357).—The crystallised body melting at  $90^{\circ}$  which R. Schiff obtained by heating pyrroline with acetic anhydride (Abstr., 1878, 216) was regarded by him as acetyl-pyrroline, in which the acetyl-group took the place of the hydrogen in the imidogen-group of the pyrroline-molecule, that is, as represented by the formula



show that in the compound thus prepared the acetyl-group is directly attached to a carbon-atom, as represented by the formula



compounds is designated as *acetyl-pyrroline*, the former as *pseudoacetyl-pyrroline*. These two compounds are formed together by the action of acetic anhydride on pyrroline; the latter, however, in much the larger quantity. They may be prepared and separated by heating

pyrroline with acetic anhydride and recently fused sodium acetate in an oil-bath, and distilling the resulting black semi-solid mass in a water-bath under reduced pressure; treating the yellow and brown crystalline residue thereby obtained with water; and distilling it in a current of steam. An oil heavier than water then passes over, and when this oil begins to deposit crystals on cooling, the operation is discontinued. The red-brown liquid then remaining in the flask contains in solution nearly the whole of the pseudoacetyl-pyrroline, provided the quantity of water is sufficient; if not, more must be added and the entire solution boiled with animal charcoal. The filtered liquid after 24 hours deposits the pseudoacetyl-pyrroline in very fine needles several centimeters long, which are easily purified by two or three crystallisations from boiling water. The remainder of the pseudoacetyl-pyrroline may be extracted from the aqueous solution by means of ether.

Pseudoacetyl-pyrroline melts at  $90^{\circ}$ , boils at  $220^{\circ}$ , and agrees in its other physical properties with the body described by Schiff. It is not, however, resolved into acetic acid and pyrroline by boiling with potash, as stated by Schiff, but the solution on cooling deposits a white solid mass, which is perhaps the potassium-compound; it dissolves on dilution with water, and ether extracts from the solution unaltered pseudoacetyl-pyrroline. On mixing a solution of pseudoacetyl-pyrroline in boiling water with a strong solution of silver nitrate and adding a few drops of ammonia, a white crystalline precipitate is formed of the silver salt  $C_4H_2\overline{Ac} : NAg$ . This reaction shows distinctly that the acetyl-radicle has entered into the nucleus of the pyrroline, and that the imidogen-group  $NH$  has remained unaltered.

By oxidation with potassium permanganate, pseudoacetyl-pyrroline is converted into the potassium salt of an acid having the composition  $C_6H_5NO_3 = C_4H_5(CO.COOH) : NH$ . This acid may be separated from the solution by acidulation with dilute sulphuric acid, and on agitating the liquid with ether, evaporating the ether, and crystallising the residue from boiling benzene, the acid separates in groups of slightly yellow needles, which give off their water in the exsiccator, and have the composition of an *acetyl-pyrroline-carboxylic acid*,  $C_6H_5NO_3, H_2O$ . The dehydrated acid has a deep yellow colour, dissolves in boiling benzene, and separates from the solution after treatment with animal charcoal, in groups of very thin yellow needles, which begin to decompose at  $113-115^{\circ}$  without showing any fixed melting point; when immersed in water they instantly turn white. They are slightly soluble in cold water and dissolve in hot water, forming a slightly yellow solution, which gives a deep red colour with ferric chloride, and does not precipitate normal lead acetate. Heated with slaked lime, it appears to yield pyrroline, as indicated by the odour of the escaping vapours, and the reaction with a deal-shaving moistened with hydrochloric acid. A highly characteristic reaction is exhibited on boiling the acid with hydrochloric acid, a very deep carmine-red solution being thereby produced, somewhat like a solution of eosin. On adding a base, a greenish-yellow colour is produced, changing to red on acidification. The aqueous acid treated with silver nitrate yields a white crystalline precipitate of the salt

$C_4H_3(CO.COOAg)NH$ , which dissolves in boiling water, and separates on cooling in colourless needles.

ACETYL-PYRROLINE,  $C_4H_4N.C_2H_3O = \overline{Ac}N \begin{array}{c} \text{CH.CH} \\ | \quad || \\ \text{CH.CH} \end{array}$ , is the oil which

passes over on distilling with steam the product of the action of acetic anhydride and sodium acetate on pyrroline. It is purified by distillation, and passes over between  $160^\circ$  and  $200^\circ$ ; a small portion which distils above that temperature and solidifies completely on cooling consists of pseudoacetyl-pyrroline, which is slightly volatile with vapour of water. After a long fractionation of the liquid at  $160-200^\circ$ , a portion is obtained which boils constantly at  $176-180^\circ$ , the greater part at  $177-178^\circ$ . This portion consists of normal acetyl-pyrroline. It may be obtained in larger quantity by the action of acetic chloride on potassium-pyrroline.

Acetyl-pyrroline boils at  $177-178^\circ$ . It has a characteristic odour; is nearly insoluble in water; gives a white precipitate with aqueous mercuric chloride; and dissolves in aqueous silver nitrate, which it reduces after some time. Its vapour reddens a chip of wood moistened with hydrochloric acid; this acid also resinifies the compound. Acetyl-pyrroline dissolves in aqueous potash, and when boiled therewith, is quickly resolved into acetic acid and pyrroline.

ACTION OF BROMINE ON PSEUDOACETYL-PYRROLINE.—Schiff describes an addition-compound obtained by the action of bromine (1 mol.) on pseudoacetyl-pyrroline dissolved in glacial acetic acid. The authors, however, have obtained by this reaction only substitution-products. The action of bromine in molecular proportion on pseudoacetyl-pyrroline yields a mixture of compounds very difficult to separate. The following methods yield better results:—

*Monobromopseudoacetyl-pyrroline*,  $C_6H_5BrNO = C_6H_2Br\overline{Ac}NH$ , is formed, together with the dibromo-compound, by dissolving pseudoacetyl-pyrroline (10 g.) in a slight excess of glacial acetic acid, and adding bromine (14 g.) dissolved in a small quantity of the same liquid, whereupon a white precipitate is formed, consisting of  $C_6H_5BrNO$ , while  $C_6H_4Br_2NO$  remains in solution. The monobromo-compound crystallises from boiling alcohol in small white needles, which turn yellow on exposure to light, and melt at  $118-120^\circ$ .

*Dibromopseudoacetyl-pyrroline*,  $C_4H_5Br_2NO = C_4HBr_2\overline{Ac}NH$ , is prepared by adding 2 mols. bromine to 1 mol. of the base, both dissolved in glacial acetic acid, pouring the liquid into water, and dissolving the resulting white precipitate in boiling alcohol with addition of animal charcoal. The filtered liquid on cooling deposits small white needles, which after a few crystallisations melt at  $145-147^\circ$ , and have a composition approximating to the formula  $C_6H_5Br_2NO$ , but still contain small quantities of a less highly brominated compound, from which the authors have not yet been able to separate it. The pure dibromo-compound is, however, easily obtained by evaporating the alcoholic mother-liquors to dryness, and crystallising the residue from boiling water, in which it is sparingly soluble, with addition of animal charcoal. The liquid on cooling deposits the dibromo-compound in small white needles, which turn yellow on exposure to light,

and after a few crystallisations melt at 143—144°. The mother-liquors contain traces of unaltered pseudoacetyl-pyrroline. The mono- and di-bromo-compounds dissolve readily in aqueous potash, and are precipitated therefrom unaltered on addition of an acid.

*Pentabromopseudoacetyl-pyrroline*,



is formed on adding bromine (4 mols.) to a solution of pseudoacetyl-pyrroline (1 mol.) in glacial acetic acid, and gently heating the resulting red liquid on the water-bath to complete the reaction. The solution, if an excess of glacial acetic acid has been avoided, deposits the pentabromo-compound on cooling in small colourless needles, which may be purified by a few crystallisations from boiling glacial acetic acid. They melt at 200°. The mother-liquor contains less highly brominated compounds, which may be precipitated by water.

The sixth disposable atom of hydrogen in pseudoacetyl-pyrroline cannot be replaced by bromine by working in the manner above described even with larger quantities of bromine; but this final substitution, might perhaps be effected by heating in sealed tubes.

H. W.

**Derivatives of Pyrocoll.** By G. L. CIAMICIAN and P. SILBER (*Ber.*, 16, 2388—2399).—*Tetrabromopyrocoll*,  $\text{C}_{10}\text{Br}_4\text{H}_2\text{N}_2\text{O}_2$ , obtained by heating pyrocoll with bromine in sealed tubes at 100°, is insoluble in most solvents save glacial acetic acid, from which it crystallises in small yellow needles; it is decomposed at 250°. When heated with caustic potash, it is converted into dibromopyrrolcarboxylic acid.

*Octochloride or Perchloride of Perchloropyrocoll*,  $\text{C}_{10}\text{H}_6(\text{Cl}_8)\text{N}_2\text{O}_2$ .—In a former communication (*Abstr.*, 1882, 875) one of the authors has shown that pyrocoll is converted by the action of phosphorus chloride into *perchloropyrocoll*,  $\text{C}_{10}\text{Cl}_6\text{N}_2\text{O}_2$ , and two other bodies having the formulæ  $\text{C}_{10}\text{Cl}_{10}\text{N}_2\text{O}$  and  $\text{C}_6\text{Cl}_7\text{NO}$ . This latter compound the authors regard as perchloride of perchloropyrocoll, and assign to it the formula  $\text{C}_{10}\text{Cl}_{14}\text{N}_2\text{O}_2$ , double that assigned to it in the previous memoir. It crystallises from glacial acetic acid in large cubical crystals, which can be easily separated by mechanical means from the flat prisms of the compound  $\text{C}_{10}\text{Cl}_{10}\text{N}_2\text{O}$ .

By the action of zinc on a solution of perchloride of perchloropyrocoll in dilute acetic acid, *tetrachloropyrroline*,  $\text{C}_4\text{Cl}_4\text{NH}$ , is formed. It crystallises from light petroleum in long silky needles, melting at 110°, easily soluble in alcohol and ether, but only sparingly in water. It is very volatile, and emits an odour resembling that of tetraiodopyrroline. In its properties it resembles those of a weak acid, and gives a white precipitate with ammoniacal solutions of silver nitrate.

In explanation of the formation of this substance, the authors suppose, first, that the perchloride takes up water to form the tetrachloride of trichloropyrroline-carboxylic acid, and that this is then resolved into carbonic anhydride and tetrachloride of trichloropyrroline; the latter is converted into tetrachloropyrroline by nascent hydrogen. This series of reactions is represented as follows:—

- (1.)  $C_{10}Cl_6(Cl_8)N_2O_2 + H_2O = 2C_4Cl_3(COOH)(Cl_4)NH.$
- (2.)  $C_4Cl_3(COOH)(Cl_4)NH = CO_2 + C_4Cl_3H(Cl_4)NH.$
- (3.)  $C_4Cl_3H(Cl_4)NH + 2H = C_4Cl_4NH + 3HCl.$

When perchloride of perchloropyrocoll is heated with dilute acetic acid in sealed tubes at  $130^\circ$ , it is resolved into hydrochloric acid, carbonic anhydride, and a compound having the formula  $C_4Cl_2O_2NH$ , which is either a *dichloromaleimide* or *dichlorofumarimide*. The formation is represented by the following equations:—

- (1.)  $C_{10}Cl_6(Cl_8)N_2O_2 + 2H_2O = 2C_4Cl_3H(Cl_4)NH + CO_2.$
- (2.)  $C_4Cl_3H(Cl_4)NH + 2H_2O = C_4Cl_2O_2NH + 5HCl.$

(Comp. this vol., p. 176.)

This same imide is obtained by the action of chlorine on succinimide at  $160^\circ$ . It crystallises from water in long needles melting at  $179^\circ$ . With ammoniacal silver nitrate solutions, it gives a precipitate of an argentic ammonium compound,  $C_4Cl_2O_2N.NH_3Ag$ . A compound, which is either monochlorofumarimide or monochloromaleimide,  $C_4ClHO_2NH$ , is formed, together with this dichloro-derivative, when succinimide is treated with chlorine. It crystallises in large colourless shining leaflets melting at  $131^\circ$ .

Caustic potash converts the imide  $C_4Cl_2O_2NH$  into a deliquescent acid, which is easily soluble in alcohol, ether, and benzene, and is probably dichloromaleic acid,  $C_4Cl_2H_2O_4$ . When heated, it yields a compound less soluble in water, probably the anhydride. When the dichloromaleimide is heated with water in sealed tubes at  $125^\circ$ , it is resolved into carbonic anhydride, ammonia, and  $\alpha$ -dichloroacrylic acid.

The conversion of the perchloride of perchloropyrocoll into dichloromaleimide suggested the possible synthesis of tetrachloropyrroline from the imide, which the authors have carried into effect by acting on the imide with phosphorus pentachloride, taking up with ether, and subsequent treatment of the ethereal extract with zinc-dust and water.

P. P. B.

**Oxymethylene and Formaldehyde.** By B. TOLLENS (*Landw. Versuchs.-Stat.*, 29, 355—392).—The preparation and properties of formaldehyde have been studied by numerous authors. The chief interest which attaches to this subject is that very possibly formaldehyde is the first assimilation-product of carbonic anhydride in the vegetable organism, and is afterwards converted by polymerisation into the various carbohydrates which form the greater proportion of the plant substance. The author made use of Hofmann's method, the oxidation of methyl alcohol by platinum foil. The best results were obtained when the water-bath in which the methyl alcohol was heated was kept at the temperature of  $54$ — $55^\circ$ . The quantity formed was, however, always small, and averaged about 2 per cent. of the total distillate; it was estimated by an ammoniacal solution of equal parts of silver nitrate and caustic soda. The distillates can be concentrated by further distillation, but the richest product obtained by this method only contained 11.3 per cent. formaldehyde. By drying

over sulphuric acid pure oxymethylene may however be obtained, although this method is attended with considerable loss. The vapour-density of oxymethylene was determined, and found to correspond with the formula  $\text{CH}_2\text{O}$ . Various ammoniacal solutions of silver nitrate were used for the exact quantitative estimation of oxymethylene, but no perfectly satisfactory method could be found.

Heated with alkalis or alkaline earths, oxymethylene yields methyl alcohol and formic acid. When the crude distillate of formaldehyde is heated with baryta-water, a yellowish precipitate is thrown down; after freeing this from barium, an amorphous syrup is left behind, which strongly reduces Fehling's solution, and on analysis gives numbers approximating to the formula  $\text{C}_6\text{H}_{10}\text{O}_5$ . When it is heated with sulphuric acid, formic and lactic acids are formed; the latter was converted into its zinc salt and analysed. The syrup has no action on polarised light, does not undergo fermentation, and yields no lævulinic acid when treated with mineral acids. In these properties it agrees with the methylenitan obtained by Butlerow.

In certain preparations of this syrup, small crystals were obtained, but the author is of opinion that they were due to the presence of ethyl alcohol, as they were never formed when perfectly pure methyl alcohol was employed.

J. K. C.

**Thioaldehyde and Carbovaleraldine.** By L. GUARESCHI (*Gazzetta*, 13, 500).—When thioaldehyde is oxidised with potassium permanganate it yields sulphuric, acetic, and ethyldenesulphuric acids, together with oxysulphides, including the compound  $\text{C}_6\text{H}_{12}\text{S}_2\text{O}_3$ . By oxidising the same body with zinc permanganate, the author obtained sulphuric acid, acetic acid, and the oxysulphides  $\text{C}_6\text{H}_{12}\text{S}_3\text{O}_5$ ,  $\text{C}_6\text{H}_{12}\text{S}_3\text{O}_4$ , and  $\text{C}_6\text{H}_{12}\text{S}_3\text{O}_2$ . The formation of ethyldenesulphuric acid and the oxysulphides points to the conclusion that solid thioaldehyde contains three  $\text{C}_2\text{H}_4\text{S}$ -groups joined together by sulphur-atoms, as represented

by the formula 
$$\begin{array}{c} \text{CHMe}-\text{S}-\text{MeHC} \\ | \qquad \qquad | \\ \text{S}-\text{CHMe}-\text{S} \end{array}$$

Carbovaleraldine is converted by ferric chloride into thiocyanic acid; by potassium permanganate into hydrocyanic, sulphuric, and valeric acids; and by ferric chloride and excess of hydrochloric acid into thiocarbamic acid. It therefore behaves like carbothialdine, and may be regarded as the thiocarbamate of valerilidene,



These and preceding experiments tend to confirm the general formula  $\text{NH}_2.\text{CS}.\text{S}.\text{N}(\text{C}_n\text{H}_m)_2$ , proposed by Mulder for the carbothialdines.

H. W.

**Preparation and Reactions of Crotonaldehyde.** By S. B. NEWBURY (*Amer. Chem. J.*, 5, 112—114).—Aldehyde (1 vol.) or paraldehyde is mixed with water (1 vol.) and concentrated hydrochloric acid (2 vols.), the liquid being cooled during mixing, and then allowed to remain for some days at the ordinary temperature until the mixture has become quite dark and opaque. On neutralising

it with sodium carbonate, it yields a thick oily layer, which after some hours becomes thick and opaque. The neutralised liquid is separated from the oily layer, repeatedly shaken with ether, the ethereal liquid evaporated, and the residue distilled under a pressure of 2 cm. of mercury, when nearly pure aldol passes over between  $90^{\circ}$  and  $110^{\circ}$ ; the maximum yield of crotonaldehyde is obtained when this aldol is heated in an oil-bath at  $140^{\circ}$ . Pure crotonaldehyde boils at  $105^{\circ}$ . As shown by Kekulé (this Journal, 1872, 616), crotonaldehyde yields dichloropseudobutylene when treated with phosphoric chloride. By the action of bromine on this chloride, *dichloropseudobutylene bromide*,  $\text{CMeHBr.CHBr.CHCl}_2$ , is obtained as a heavy oily liquid, which is decomposed when heated above  $100^{\circ}$ . On boiling it with dilute potassium carbonate, carbonic anhydride is evolved, but the removal of the halogens is only partial. A fraction,  $115\text{--}120^{\circ}$ , gave numbers approximating to those required for  $\text{C}_4\text{H}_6\text{BrClO}$ . Crotonaldehyde unites directly with bromine to form a heavy oily liquid of the formula  $\text{CHMeBr.CHBr.CHO}$ . Its vapour is very irritating. It is decomposed when heated. Attempts to replace the bromine by hydroxyl-groups were unsuccessful.

A. J. G.

**Nonoic Acids from different Sources.** By E. SCHMIDT (*Ber.*, 16, 2590).—An examination of the nonoic acids obtained from the following sources shows that they are identical and of normal constitution:—1, from normal octyl alcohol from heracleum-oil; 2, from the oxidation of oleic acid; 3, from the oxidation of methyl nonyl ketone; 4, from the distillate of the leaves of *Pelargoneum roseum*; 5, from the fusel-oil of beet-molasses; and 6, from undecylenic acid.

A. K. M.

**A New Acid Isomeric with Crotonic Acid.** By R. FITTIG and F. ROEDER (*Ber.*, 16, 2592—2593).—A further study of the acid previously obtained by the authors (*Abstr.*, 1883, 730) leaves little doubt as to its being *vinylmalonic acid*,  $\text{CH}_2\text{:CH.CH}(\text{COOH})_2$ . It combines with hydrobromic acid to form bromethylmalonic acid, which is decomposed by boiling water into hydrobromic acid and *butyrolactone-carboxylic acid*,  $\text{COOH.CH} \begin{smallmatrix} \text{CH}_2 \\ \text{COO} \end{smallmatrix} \text{CH}_2$ ; at  $120^{\circ}$  this is decomposed into carbonic anhydride and butyrolactone. The properties of the acid,  $\text{C}_4\text{H}_6\text{O}_2$ , obtained by the distillation of vinylmalonic acid differ from those of isocrotonic acid. It crystallises at a low temperature, melts at  $18\text{--}19^{\circ}$ , and boils at  $180\text{--}181^{\circ}$ . The authors think it probable that the formula  $\text{CH}_2\text{:CH.CH}_2\text{COOH}$ , represents the constitution of this new acid and not that of isocrotonic acid, and that the isomerism of the latter with crotonic acid is of the kind frequently observed amongst unsaturated acids and unexplained by our present formulæ; this is confirmed by the results obtained by Friedrich (*Abstr.*, 1883, 968) from the chlorisocrotonic acids.

A. K. M.

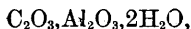
**Preparation of Glycollic Acid from Glycerol.** By H. KILIANI (*Ber.*, 16, 2414—2416).—The author has already shown that several glucoses and nearly allied compounds yield glycollic acid when oxidised by silver oxide, and has recommended the oxidation of in-



verted sugar as a method for preparing this compound (*Annalen*, **205**, 191). The acid can, however, be more easily obtained by oxidising glycerol with silver oxide in presence of an alkali. For this purpose 10 grams of glycerol are mixed with 200 c.c. of water and 6 grams of slaked lime added, to this the oxide of silver obtained from 60 grams of silver nitrate is next added, and the whole heated at 60° for some four hours. The product is treated with carbonic anhydride and filtered; on concentrating the filtrate, calcium glycolate separates out. P. P. B.

**Optically Active Glyceric and Lactic Acids.** By J. LEWKOWITSCH (*Ber.*, **16**, 2720—2721).—Solutions of ammonium glycerate and ammonium lactate exposed to the action of *Penicillium glaucum* for several weeks become optically active. The glyceric acid solution becomes lævo- and the lactic acid solution dextro-rotate. The optically active acids have not yet been isolated. W. C. W.

**Tribasic Aluminium Oxalate.** By MATHIEU-PLESSY (*Compt. rend.*, **97**, 1033).—An aqueous solution of oxalic acid attacks aluminium at 200°, and also attacks tribasic aluminium sulphate, the product of the action being an oxalate of the composition—



which may be regarded as kaolin in which oxalic acid has replaced silica equivalent for equivalent, thus furnishing a further example of the analogy between carbon and silicon. C. H. B.

**Monethyl Oxalate.** By R. ANSCHÜTZ (*Ber.*, **16**, 2412—2414).—This compound, which has hitherto remained unisolated, is obtained by heating equal quantities of dehydrated oxalic acid and absolute alcohol at 135°. After cooling, the crude oxalate is decanted from the oxalic acid and submitted to rectification under reduced pressure. *Monethyl oxalate*,  $\text{C}_2\text{O}_4\text{HEt}$ , is a transparent, colourless liquid, sp. gr. at 20° = 1.2175 (water at 4° = 1); it has a strongly acid reaction; by water, it is resolved into ethyl alcohol and oxalic acid. It boils at 117° under a pressure of 15 mm., and decomposes when distilled under ordinary pressure, forming ethyl formate and diethyl oxalate, thus:  $\text{C}_2\text{O}_4\text{EtH} = \text{H.COOEt} + \text{CO}_2$ ;  $2\text{C}_2\text{O}_4\text{EtH} = \text{C}_2\text{O}_4\text{Et}_2 + \text{CO}_2 + \text{CO} + \text{H}_2\text{O}$ . Monethyl oxalate can also be prepared from crystallised oxalic acid and alcohol by a method similar to the one used by the author and Pictet in preparing the ethereal salts of tartaric acid. P. P. B.

**Identity of Isopropylsuccinic Acid with Pimelic Acid from Camphoric Acid.** By E. HJELT (*Ber.*, **16**, 2621—2623).—On oxidising isopropylsuccinic acid, no terebic acid was formed, as might be expected if the assumed constitution of this acid is correct. When treated with alkaline potassium permanganate in calculated quantity a portion becomes completely burnt, another portion remaining unattacked. When heated with nitric acid (4:1), it remains unaltered.

In its properties, isopropylsuccinic acid agrees with pimelic acid, and the properties of its salts are also identical with those of the salts of the latter acid, as described by Hlasiwetz, Grabowski, and Kachler. It dissolves readily in water and in ether, melts at  $114^{\circ}$ , and yields an anhydride at higher temperatures. The calcium salt,  $C_7H_{10}O_4Ca$ , is anhydrous, and is precipitated as a sandy powder; the barium salt is very readily soluble; the silver salt is sparingly soluble. The identity is further confirmed by a crystallographic examination of this acid, the measurements closely agreeing with those of Ditscheiner and Zepharovich.

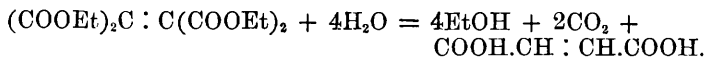
A. K. M.

**Reduction of Pyrotartaric Chloride.** By E. HJELT (*Ber.*, 16, 2624).—Saytzeff having obtained butyrolactone by the reduction of succinic chloride (*Annalen*, 171, 258), the author has tried the reaction with pyrotartaric chloride. This is a colourless oil boiling at  $190-195^{\circ}$ ; it is gradually decomposed by water with formation of pyrotartaric acid. When its ethereal solution is acted on by glacial acetic acid and sodium-amalgam, the ether-extract evaporated, treated with water and potassium carbonate, and then extracted with ether, a neutral oil is obtained boiling for the most part at  $203-205^{\circ}$ . It has not been obtained pure, the analytical results agreeing only approximately with the formula  $C_5H_8O_2$ ; it has an odour like that of a lactone, dissolves in 5–6 parts water, and does not solidify in a freezing mixture of ice and salt. Boiled with barium hydroxide solution, it yields a gummy barium salt, which when dried at  $100^{\circ}$  has a composition agreeing with the formula  $(C_5H_7O_2)_3Ba$ .

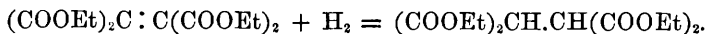
The constitution of the chlorides which yield lactones may be assumed to be analogous to that of phthalic chloride.

A. K. M.

**Ethyl Dicarbonditetracarboxylate.** By M. CONRAD and M. GUTHZEIT (*Ber.*, 16, 2631–2632).—This is best prepared by adding the calculated quantity of sodium to a mixture of ethyl chloromalonate (19.4 grams) and ether (free from water and alcohol). After about 20 hours, the ether is separated by distillation, the unaltered sodium removed, and the product mixed with water; the ethyl dicarbonditetracarboxylate obtained is purified by crystallisation from alcohol. When it is heated in sealed tubes with alcohol and hydrochloric acid, first at  $150^{\circ}$  and subsequently at  $190^{\circ}$ , fumaric acid is formed according to the equation:—



By the action of zinc-dust and hydrochloric acid on an alcoholic solution of ethyl dicarbonditetracarboxylate, ethyl acetylenetetracarboxylate melting at  $76^{\circ}$  is produced:—

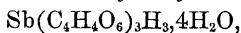


A. K. M.

**Attempts to obtain Tartronic Acid from Glycerol, and Tartaric Acid from Erythrol by Electrolytic Oxidation.** By D.

BIZZARRI and G. CAMPANI (*Gazzetta*, **13**, 490—492).—The experiments did not lead to the expected results. H. W.

**Antimony Tartrates.** By F. W. CLARKE and C. S. EVANS (*Ber.*, **16**, 2379—2387).—When antimony trioxide is dissolved in a considerable excess of tartaric acid, and the solution evaporated, it yields a well defined crystalline salt. It is not, however, always easy to obtain this compound, gummy amorphous masses being obtained in some cases. These crystals prove to be *antimony trihydric tartrate*,

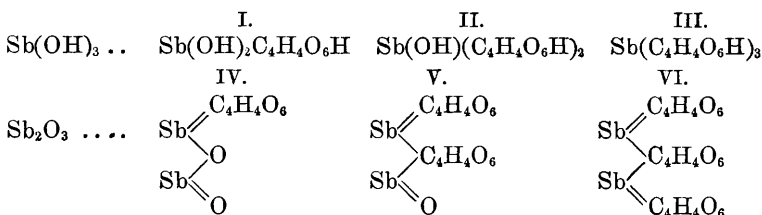


This salt crystallises in rosettes of white needles, easily soluble in water. It is strongly acid, decomposing carbonates with evolution of carbonic anhydride. The *normal antimony tartrate*,  $\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_3\cdot 6\text{H}_2\text{O}$ , is obtained by adding sodium carbonate to a solution of the trihydric tartrate, and then precipitating with alcohol; it forms a heavy white precipitate, easily soluble in water. In the cold, sodium carbonate has no action on it, but on boiling, a white precipitate is formed. Attempts to prepare double salts from antimony trihydric tartrate were unsuccessful.

By evaporating to dryness a saturated solution of antimony trioxide in tartaric acid, a non-crystalline residue was obtained having the composition  $\text{Sb}(\text{OH})\text{H}_2(\text{C}_4\text{H}_4\text{O}_6)_2$ , which may also be represented as  $\text{Sb}(\text{C}_4\text{H}_5\text{O}_6)_2\text{OH}$ . Its aqueous solution when treated with alcohol yields a white precipitate of a compound  $\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2\cdot 0.6\text{H}_2\text{O}$ .

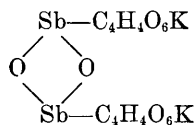
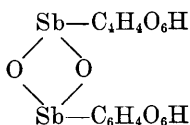
When the aqueous solution of this tartrate is allowed to evaporate, it yields a yellow scaly mass containing 16.39 per cent. of water, and when heated at  $170^\circ$  loses another molecule of water, and leaves a residue of two molecules of  $\text{Sb}\equiv\text{C}_4\text{H}_3\text{O}_6$ . These results indicate the existence of two salts, having the formulæ  $\text{SbC}_4\text{H}_3\text{O}_6$  and  $\text{SbC}_4\text{H}_5\text{O}_7$  respectively.

The results of this investigation indicate the existence of two series of antimony tartrates, one derived from ortho-antimonic acid,  $\text{Sb}(\text{OH})_3$ , and the other from antimony trioxide,  $\text{Sb}_2\text{O}_3$ ; the constitution of these salts is represented as follows:—

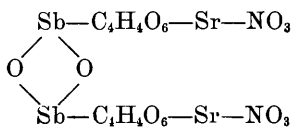
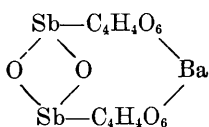


Of these, the antimony trihydric tritartrate (III), the antimony tritartrate (VI), and the antimony ditartrate, are described in the foregoing. The probable existence of II, antimony dihydric ditartrate, is also demonstrated. Attempts to prepare the compounds I and IV have not yielded altogether satisfactory results.

The authors consider that in its tartrates, antimony behaves just as any other trivalent metal, and the supposed existence in them of a radicle ( $\text{SbO}$ ) is altogether unnecessary. There are cases, as for instance in tartar emetic, where the Sb atom and the oxygen atom are united, still the composition of these may be explained without presupposing the existence of the radicle ( $\text{SbO}$ ). Tartar emetic may be represented as derived from a tartarantimonious acid, thus:—



a view by which the composition of barium antimony tartrate and of the double salt of strontium antimony tartrate and strontium nitrate can be easily explained, as shown in the following formulæ:—



P. P. B.

**Oxidation of Benzene Derivatives with Potassium Ferricyanide.** By W. A. NOYES (*Amer. Chem. J.*, 5, 97—105).—The presence of negative atoms or groups in many benzene derivatives exerts a powerful influence on the oxidation of hydrocarbon groups attached to the same benzene ring. Experiments, so far, seem to show that a hydrocarbon-group in the ortho-position relatively to the negative atom or group, is not oxidised at all, or only in small amount, by chromic acid; that nitric acid can oxidise a group in the ortho-position, but if there is a choice, will, in preference, oxidise groups in the meta- or para-position. Caustic potash, in the one class of compounds for which it has been used, oxidises groups in the ortho-position; potassium permanganate in alkaline solution oxidises groups in all three positions, but where there is a choice would seem to oxidise the group in the ortho-position by preference.

In order to ascertain if another alkaline oxidising agent would behave similarly to the two last mentioned, the author has investigated the action of potassium ferricyanide in alkaline solution on the nitro- and bromo-toluenes. Ortho-, nitro-, and paranitro-toluene are both readily oxidised to the corresponding nitrobenzoic acids, there being no indication as to which is oxidised more easily. Para-bromotoluene is only oxidised with great difficulty with alkaline ferricyanide, whilst orthobromotoluene appears to be scarcely attacked. For comparison, toluene was treated with alkaline ferricyanide, and found to be only slightly attacked by it.

A. J. G.

**Metaisopropylmethylbenzene.** By H. E. ARMSTRONG and A. K. MILLER (*Ber.*, 16, 2748—2750).—When pure metaisocymene is dissolved in warm sulphuric acid, and the solution neutralised with

barium carbonate, the barium salt of  $\alpha$  metaisocymenesulphonic acid is deposited, and the mother-liquor contains a more soluble salt, which readily crystallises in prisms of the composition  $(C_{10}H_{13}SO_3)_2Ba + 9H_2O$ . According to Kelbe (*Annalen*, **210**, 30) the  $\beta$  barium salt is deposited from the concentrated syrupy solution in glistening plates containing 1 mol.  $H_2O$ . The calcium salt resembles the barium salt and crystallises with  $5\frac{1}{2}$  mols.  $H_2O$ . The potassium salt forms long prisms containing  $2\frac{1}{2}$  mols.  $H_2O$ . W. C. W.

**Action of Chlorine on Boiling Cymene.** (Preliminary Notice.)

By G. ERRERA (*Gazzetta*, **13**, 421—422).—The action of chlorine on cymene vapour gives rise to a liquid resolvable by a few fractional distillations into three portions, the first passing over below  $195^\circ$ , and containing a considerable quantity of unaltered cymene, the second boiling at  $225$ — $229^\circ$ , the third above  $255^\circ$ . This last portion is rapidly decomposed by boiling, but on distilling it with steam, a heavy oily liquid passes over, apparently consisting of a mixture of di- and mono-chlorocymene. The more abundant fraction, boiling at  $225$ — $229^\circ$ , is a liquid heavier than water, decomposing on distillation, with evolution of hydrochloric acid, and consisting, as shown by analysis, of monochlorocymene or cymyl chloride,  $C_{10}H_{13}Cl$ , identical with that which Paternò and Spica obtained by the action of hydrochloric acid on cymyl alcohol\* (Abstr., 1880, 106). Cymyl chloride, heated in a reflux apparatus with lead nitrate, is converted into cumic aldehyde, which in its turn is oxidised to terephthalic and cumic acids.

Cymyl chloride is decomposed by boiling, yielding hydrochloric acid and a fluorescent hydrocarbon,  $C_{20}H_{24}$ , of very high boiling point.

H. W.

**Two Butyltoluenes Occurring in Rosin Spirit.** By W. KELLE and A. BAUR (*Ber.*, **16**, 2559—2566).—Kelbe (Abstr., 1881, 809) obtained a hydrocarbon of the formula  $C_{11}H_{18}$  from rosin spirit; this yielded isophthalic acid on oxidation, and he therefore assumed it to be either a methylbutylbenzene or an ethylpropylbenzene. The authors now find it to be *metaisobutyltoluene*,  $C_6H_4Me.CH_2.CHMe_2$ , and they have also obtained an isomeric hydrocarbon, namely, *parabutyltoluene*. Metaisobutyltoluene, obtained on heating its lead sulphonate at  $150^\circ$  with concentrated hydrochloric acid, is a colourless strongly refracting liquid of agreeable odour, boiling at  $186$ — $188^\circ$ . Its sulphonic acid crystallises in small very deliquescent scales, melting at  $75$ — $76^\circ$ . The *barium salt*,  $(C_{11}H_{15}SO_3)_2Ba \cdot H_2O$ , forms small lustrous scales, sparingly soluble in cold, more readily in hot water, very sparingly in absolute alcohol; the *lead salt*,  $(C_{11}H_{15}SO_3)_2Pb \cdot 3H_2O$ , forms large nacreous plates, much more readily soluble in hot than in cold water; the *potassium salt*,  $C_{11}H_{15}SO_3K \cdot H_2O$ , crystallises in large moderately soluble nacreous plates, and the *sodium salt*,  $C_{11}H_{15}SO_3Na \cdot H_2O$ , in easily soluble lustrous needles; the *copper salt*,  $(C_{11}H_{15}SO_3)_2Cu \cdot 4H_2O$ , crystallises in large blue lustrous plates, readily soluble in water.

\* Commonly, but incorrectly, called cumic alcohol or cumyl alcohol; the proper name of the radicle  $C_{10}H_{13}$  is *cymyl*.—H. W.

*Metaisobutyltoluenesulphonamide*,  $C_{11}H_{15}.SO_2.NH_2$ , crystallises in small lustrous scales melting at  $74-75^\circ$ .

*Parabutyltoluene*,  $C_8H_4Me.C_4H_9$ , is separated from the crude meta-isocymene by crystallising the barium sulphonates from 50 per cent. alcohol, in which barium parabutyltoluenesulphonate is much more readily soluble than the meta-isocymene salt. Parabutyltoluene (b. p.  $176-178^\circ$ ) is a colourless, highly refracting liquid of agreeable odour; dilute nitric acid oxidises it to paratoluic acid. The *barium sulphonate*,  $(C_{11}H_{15}.SO_3)_2Ba.H_2O$ , forms small scales, sparingly soluble in water; the *lead salt*,  $(C_{11}H_{15}.SO_3)_2Pb.3H_2O$ , crystallises in small lustrous scales, sparingly soluble in cold, readily in hot water; the *potassium salt*,  $C_{11}H_{15}.SO_3K.1\frac{1}{2}H_2O$ , in small, lustrous, easily soluble scales; the *sodium salt*,  $C_{11}H_{15}.SO_3Na.2H_2O$ , in small wart-like crystals, readily soluble in water, and the *copper salt* in readily soluble bright blue wart-like crystals. *Parabutyltoluenesulphonamide*,  $C_{11}H_{15}.SO_2NH_2$ , forms large nacreous plates melting at  $113^\circ$ , and sparingly soluble in hot water. With potassium permanganate, it yields *paratolylsulphonaminic acid*,  $COOH.C_6H_3Me.SO_2NH_2$ , melting at  $242^\circ$ , sparingly soluble in water, almost insoluble in ether and in alcohol.

Metaisobutyltoluene, identical with the hydrocarbon contained in rosin-spirit, can be obtained synthetically from isobutyl bromide and toluene, in presence of aluminium bromide. A. K. M.

**Reductions with Zinc and Ammonia.** By W. G. MIXTER (*Amer. Chem. J.*, 5, 1-9).—Powdered zinc, with aqueous or alcoholic ammonia, and a small quantity of platinic chloride solution, forms a very gentle reducing agent, of which, so far, but little use seems to have been made. It was used for the reductions in the preparation of the bodies described below.

*Parazoxyacetanilide*,  $O \begin{cases} \nearrow N.C_6H_4.NH\bar{A}c \\ \searrow N.C_6H_4.NH\bar{A}c \end{cases}$ , obtained by the reduction

of paranitracetanilide in alcoholic solution, forms minute hair-like particles of a light golden-yellow colour, melts at  $275-278^\circ$ , is sparingly soluble in boiling, nearly soluble in cold alcohol. The ammoniacal mother-liquor from the preparation of this substance contains *azo-acetanilide*,  $C_{16}H_{16}N_4O_2$ ; it will be described in a future paper. By boiling parazoxyacetanilide with alcoholic potash, it yields *parazo-*

*oryaniline*,  $O \begin{cases} \nearrow N.C_6H_4.NH_2 \\ \searrow N.C_6H_4.NH_2 \end{cases}$ , as a fibrous mass which melts at  $182-$

$184^\circ$ , and is readily soluble in alcohol. The hydrochloride crystallises well from water, and is sparingly soluble in alcohol. The sulphate separates on adding sulphuric acid to a dilute solution of the base. The platinochloride,  $C_{12}H_{12}N_4O.H_2PtCl_6$ , forms long brownish-red needles. By reduction with ammonium sulphide, or with tin and hydrochloric acid, azoxyaniline yields paraphenylenediamine, showing that the azoxy- and amido-groups occupy the [1 : 4] positions.

*Metazoxybenzanilide*,  $O \begin{cases} \nearrow N.C_6H_4.NHBz \\ \searrow N.C_6H_4.NHBz \end{cases}$ , obtained by the reduction

of metanitrobenzanilide, forms a light powder of pale yellow colour; it melts at  $272^{\circ}$ , and is insoluble or nearly insoluble in alcohol, ether, and benzene. The mother-liquor, after renewed digestion with zinc, yielded the substance  $\text{NH}\bar{\text{Bz}}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , described by Bell (this Journal, 1874, 900).  
A. J. G.

**Action of Ethyl Acetoacetate on Phenylhydrazine.** I. By L. KNORR (*Ber.*, 16, 2597—2599).—This reaction is similar to that between ethyl acetoacetate and aniline, yielding a new class of compounds, the properties of which closely resemble those of  $\alpha$ -meth- $\gamma$ -hydroxyquinoline (see p. 334). According to Fischer, phenylhydrazine and ethyl acetoacetate, at the ordinary temperature, yield an oily condensation-product with liberation of water; this compound must have the formula  $\text{PhN}_2\text{H}:\text{CMe}\cdot\text{CH}_2\cdot\text{COOEt}$ . When heated on a water-bath, it yields alcohol and a substance,  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}$ , which resembles carbostyryl in many of its properties. It melts at  $127^{\circ}$ , can be distilled unchanged, and shows both basic and acid properties; it is a stronger acid than carbostyryl, dissolving in ammonia and in alkaline carbonates. To prepare it, 100 grams of phenylhydrazine are added to 125 grams of ethyl acetoacetate, the water which forms is separated, and the oily product is heated for about two hours on a water-bath, until a portion is found to solidify on cooling, or on the addition of ether. The warm mass is poured into and stirred with ether, which removes colouring matter, and the white crystalline product is then washed with ether and dried at  $100^{\circ}$ . The yield is quantitative and the product pure. It is almost insoluble in cold water, ether, and light petroleum, more readily soluble in hot water, and very readily in alcohol. It crystallises from hot water in hard prisms, and by the slow evaporation of its alcoholic solution can be obtained in crystals of diamond lustre. It yields crystalline precipitates with salts of most of the heavy metals, the ultramarine blue cobalt salt, and the orange-yellow uranium salt, being especially characteristic. Its constitution remains to be explained. An anhydride,  $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}$ , is formed, when it is heated with an excess of phenylhydrazine; this may be prepared as follows: ethyl acetoacetate (50 grams) is mixed with phenylhydrazine (60—70 grams), the water which forms separated, and the oily product heated to boiling in an oil-bath until a solid mass is obtained; on boiling this with alcohol, the anhydride is obtained pure. Heated to  $250$ — $260^{\circ}$  it turns brown and decomposes before melting. It is insoluble in most of the usual solvents; is in many respects similar to carbostyryl; dissolves in acids and bases, from which it is reprecipitated on neutralisation; it is insoluble in acetic acid and in ammonia, and is precipitated by carbonic anhydride from its alkaline solution, so that it apparently contains a hydroxyl-group.  
A. K. M.

**A New Group of Organic Bases.** By O. WIDMANN (*Ber.*, 16, 2576—2587).—By the action of acetic anhydride on amidohydroxypropylbenzoic acid (the external application of heat being avoided), acetamidohydroxypropylbenzoic acid is formed (see p. 317), but if the amido-acid is boiled with an excess of acetic anhydride, and the latter

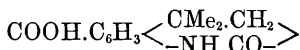
then separated by repeated evaporation with alcohol, a reddish coloured oil is obtained crystallising from alcohol in rhombic plates, melting at  $218^{\circ}$ , and insoluble in water. Its hydrochloride is extremely soluble in water, sodium acetate reprecipitating the base  $C_{12}H_{13}NO_3$  in white needles. The same compound is formed on boiling acetamidohydroxypropylbenzoic acid with hydrochloric acid, and also when acetamidopropenylbenzoic acid is boiled with hydrochloric acid. The author names it *methylcumazonic acid*; it dissolves readily in dilute acids, forming salts, and also in concentrated sulphuric acid. On distillation, it yields a tarry product having an odour like that of indole, but when cautiously heated, white needles sublime. By the action of potassium nitrite on a solution of the hydrochloride, nitrous acid is liberated, whilst needles of free methylcumazonic acid separate. When heated in a tube with ethyl iodide, it yields a syrupy substance which could not be obtained in a pure state. By evaporating a solution of the base in dilute sulphuric acid, the acid sulphate,  $C_{12}H_{13}NO_3 \cdot H_2SO_4 + H_2O$ , is obtained in slender, white, silky needles, very readily soluble in water; it loses its water of crystallisation at  $100-140^{\circ}$ . The hydrochloride crystallises in needles. The platinum-chloride,  $(C_{12}H_{13}NO_3)_2 \cdot H_2PtCl_6$ , forms lustrous four-sided plates or cubical crystals, very readily soluble in water. By the action of sodium-amalgam on a solution of methylcumazonic acid in sodium hydroxide, the compound  $C_{12}H_{15}NO_3$  is produced; it is very sparingly soluble in ether and alcohol, crystallising from the latter in slender needles, which melt at  $246^{\circ}$  and sublime at higher temperatures. This substance is identical with *acetamidocumic acid*,



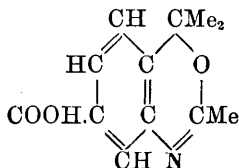
prepared by the author from nitrocumic acid. With the object of eliminating an acetyl-group from methylcumazonic acid, it was boiled with hydrochloric acid and with alcoholic potash, but with negative results. Judging from its formation from amidohydroxypropylbenzoic acid or its acetyl-derivative, methylcumazonic acid might be

assumed to have the constitution  $COOH.C_6H_3 \begin{matrix} \swarrow CMe_3 \\ | \\ \searrow N\bar{A}c \end{matrix}$ , but this for-

mula does not explain the basic character of the substance, nor the difficulty of displacing the acetyl-group: the formula



is equally unsatisfactory. Its reactions and properties can, however, be satisfactorily explained on the assumption that its constitution is—





*i.e.*, that it is formed by the abstraction of the elements of a molecule of water from acetamidohydroxypropylbenzoic acid, the carbon-atom of the propyl residue uniting with the oxygen-atom of the acetyl-group. A substance of this constitution must be a tertiary base, contains no acetyl-group, and might yield acetamidocumic acid on reduction. Its formation from acetamidopropenylbenzoic acid is more difficult to explain, the yield in this case being also less satisfactory; the hydrochloric acid may perhaps first form an addition-compound with the propenyl-group, the chlorine then separating again, but in union with the amido-hydrogen. In support of the above constitution, the author mentions the analogous formation of Ladenburg's condensation-products from orthamidophenol, and the acid anhydrides

(*Ber.*, 9, 1524) as, for example,  $C_6H_4 \begin{smallmatrix} \diagup O \diagdown \\ N \end{smallmatrix} CMe$ .

The name "methylcumazonic acid" is intended to imply that this substance is derived from cumic acid, and that it contains both nitrogen and oxygen, "cumazone" being the hypothetical parent substance  $C_6H_4 \begin{smallmatrix} CMe_2 \\ N:CH \end{smallmatrix} O$ .

*Ethylcumazonic acid*,  $COOH.C_6H_3 \begin{smallmatrix} CMe_2O \\ N:CEt \end{smallmatrix}$ , is obtained by boiling amidohydroxypropylbenzoic acid with an excess of propionic anhydride, and crystallises from alcohol in small lustrous well-formed pyramids, melting at  $202^\circ$ ; it is readily soluble in alcohol, insoluble in water. The hydrochloride crystallises in white needles, extremely soluble in water. The acid sulphate,  $C_{13}H_{15}NO_3.H_2SO_4$ , also crystallises in extremely soluble white needles. The free base dissolves readily in very dilute sulphuric acid.

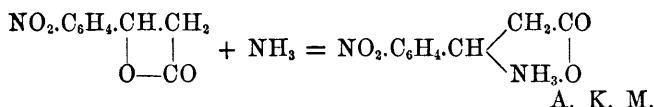
*Phenylcumazonic acid*,  $C_{17}H_{15}NO_3$ , is formed on heating amidohydroxypropylbenzoic acid with an excess of benzoic chloride at  $100-120^\circ$ , as long as hydrochloric acid is evolved, boiling the product with alcohol and subsequently with water. It melts at  $219-220^\circ$ , is insoluble in water, and separates from alcohol in transparent crystals of the formula  $2C_{17}H_{15}NO_3 + EtOH$ . The acid sulphate,  $C_{17}H_{15}NO_3.H_2SO_4 + 2H_2O$ , forms lustrous, colourless, elliptical plates, insoluble in water.

Compared with the methyl- and ethyl-derivatives, phenylcumazonic acid is a weak base. A. K. M.

**Orthonitrophenyl- $\beta$ -alanine.** By A. EINHORN (*Ber.*, 16, 2645—2651).—In describing the lactone of orthonitrophenyl- $\beta$ -lactic acid (this vol., p. 65), the author mentioned that it was converted into salts of the hydroxy-acid by warming it with alkaline hydrates or baryta. When heated with ammonia solution, it gradually dissolves, and on cooling white crystals separate; these, after recrystallisation, melt at  $197^\circ$ . The product,  $C_9H_{10}N_2O_4$ , has the composition of *orthonitrophenyl- $\beta$ -alanine*, but it neither forms metallic salts, nor does it combine with acids. In order to be able to compare it with orthonitrophenyl- $\beta$ -alanine, the author prepared the latter by dissolving orthonitrophenyl- $\beta$ -bromopropionic acid in an excess of ammonia, and

leaving the solution at rest. Crystalline scales gradually separate, and on recrystallisation from water or alcohol needles are obtained melting at  $197^{\circ}$ . The composition,  $C_9H_{10}N_2O_4$ , and mode of preparation of the product show it to be orthonitrophenyl- $\beta$ -alanine; it dissolves readily in water, alcohol, acetone, and glacial acetic acid, more sparingly in ether, chloroform, light petroleum, and carbon bisulphide. It dissolves when heated with dilute sodium carbonate solution, but not more readily than in water, and separates unchanged on cooling. When boiled with sodium or barium hydroxide, it does not yield salts, a partial decomposition taking place with formation of ammonia; attempts to obtain copper and silver salts were also unsuccessful. Orthonitrophenyl- $\beta$ -alanine crystallises unchanged from dilute or concentrated hydrochloric acid. Sulphuric acid (1 part acid and 1 part water) dissolves it in the cold, but decomposition sets in after a time. On warming it with concentrated sulphuric acid, a blue solution is obtained, and on pouring this into water a blue dye is precipitated agreeing in its reactions with indoïn. It is converted into the orthonitro- $\beta$ -lactic acid by boiling with nitrous acid. The perfect coincidence of these properties with those of the compound obtained by the action of ammonia on the lactone, prove the identity of the two substances. The *acetyl-derivative*,  $C_{11}H_{12}N_2O_5$ , is prepared by dissolving orthonitrophenyl- $\beta$ -alanine in boiling acetic anhydride; it crystallises from alcohol in splendid prisms melting at  $141-142^{\circ}$ ; it crystallises unchanged from hot water, is insoluble in cold sodium carbonate and alkali solutions, but on boiling with the latter, is decomposed with formation of orthonitrophenyl- $\beta$ -alanine. It does not yield salts when boiled with copper hydroxide or silver hydroxide, is insoluble in cold hydrochloric acid, but dissolves in hot concentrated sulphuric acid to a blue solution, which has a strong odour of acetic acid. When the alanine is boiled for about three hours with acetic anhydride, the latter separated by distillation, and the residue crystallised from alcohol, a substance,  $C_{11}H_{10}N_2O_4$ , is obtained crystallising in needles melting at  $172^{\circ}$ . It is assumed to be the *lactam of orthonitrophenyl- $\beta$ -acetylalanine*,  $NO_2.C_6H_4.CH<\begin{smallmatrix} CH_2 \\ NAc \end{smallmatrix}>CO$ . It is decomposed by dilute soda solution, with evolution of ammonia and formation of orthonitrocinnamic acid. If equal quantities of the alanine and sodium acetate are boiled with acetic anhydride, and after removal of the latter the product is crystallised from alcohol, the above lactam separates, whilst the solution contains a small quantity of a second substance, which is probably the *lactam of orthonitrophenyl- $\beta$ -alanine*,  $NO_2.C_6H_4.CH<\begin{smallmatrix} CH_2 \\ N.H \end{smallmatrix}>CO$ . It crystallises in transparent, strongly refracting, vitreous prisms, melting at about  $80^{\circ}$ , but it has not yet been obtained pure. It is moderately soluble in hot water, and is not altered by alkalis or acids.

From the chemical behaviour of orthonitrophenyl- $\beta$ -alanine, and from its ready production from the lactone or orthonitrophenyl- $\beta$ -lactic acid and ammonia, the author concludes that it is not an amido-acid, and he gives the following equation to express its formation:—

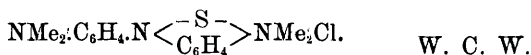


**Synthesis of Methylene-blue.** By R. MÖHLAU (*Ber.*, **16**, 2728—2730).—When nitrosodimethylaniline acts on dimethylaniline in presence of strong hydrochloric acid, the hydrochloride of the base  $\text{C}_{16}\text{H}_{19}\text{N}_3$  is obtained. The base crystallises in prisms which melt at  $215^\circ$ . Methylene-blue is produced by reducing the hydrochloride with sulphuretted hydrogen and oxidising the product with ferric chloride. The base  $\text{C}_{16}\text{H}_{19}\text{N}_3$  is decomposed by reducing agents, such as zinc-dust, into paramidomethylaniline and dimethylaniline. By oxidising these products of reduction, dimethylaniline-green is formed.

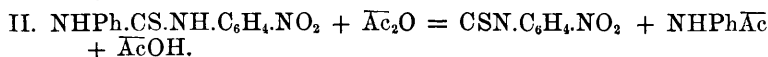
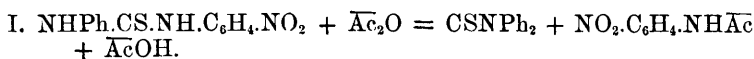
Sulphuretted hydrogen converts dimethylaniline-green into leuco-dimethylaniline-green and methylene-white, and by alternate reduction with sulphuretted hydrogen and oxidation with ferric chloride, dimethylaniline-green is converted into methylene-white and methylene-blue. As methylene-white has the constitution



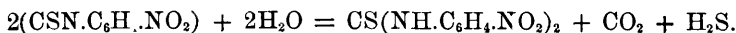
the hydrochloride of methylene-blue is probably



**Metanitrophenylthiocarbimide.** By H. STRUDEMANN (*Ber.*, **16**, 2331—2335).—The production of this compound by the action of hot glacial acetic acid on metanitrothiocarbamide has already been described (*Abstr.*, 1883, 801). In this communication, the author gives an account of a detailed examination of the reaction taking place in its production, which may be represented by the following equations:—



The presence of phenylthiocarbimide, metanitroacetanilide, metanitrophenylthiocarbimide, and acetanilide was satisfactorily demonstrated amongst the products of the reaction. Two other substances are also produced, viz., metanitrodiphenylthiocarbamide melting at  $160$ — $161^\circ$ , and a substance having the same composition as metanitrophenylthiocarbimide; the formation of the former resulting from the action of water on metanitrophenylthiocarbimide, thus:—



Phenylthiocarbimide undergoes a similar change when heated with water in sealed tubes at  $100^\circ$ , giving diphenylthiocarbamide, carbonic anhydride, and sulphuretted hydrogen.

These secondary reactions show that in the preparation of metanitrophenylthiocarbimide, distillation in a current of steam should be avoided, and the purification by crystallising from glacial acetic acid and carbon bisulphide is to be preferred.

Metanitrophenylthiocarbimide is also formed by the action of glacial acetic acid on dinitrophenylthiocarbimide. It crystallises in long flexible needles melting at  $60.5^\circ$ , and boiling at  $275-280^\circ$ ; it is soluble in alcohol, ether, benzene, and carbon bisulphide. Attempts to reduce the "nitro-group" have failed; the alcoholic solution of this compound yields nitraniline when treated with sulphuretted hydrogen.

The following derivatives of metanitrophenylthiocarbimide have been prepared:—*Metanitrophenylparatolylthiocarbimide*,



pale yellow needles melting at  $173^\circ$ , and sparingly soluble in water, benzene, and ether, easily soluble in alcohol and glacial acetic acid. *Metanitrophenylparaoxyphenylthiocarbimide*,



crystallises in white needles melting at  $152^\circ$ . *Metanitrophenylorthonitroparatolylthiocarbimide*,  $\text{NO}_2.\text{C}_6\text{H}_4.\text{NH}.\text{CS}.\text{NH}.\text{C}_6\text{H}_3\text{Me}.\text{NO}_2$  [1 : 2 : 4], crystallises in yellow needles melting at  $188^\circ$ . P. P. B.

**Orthonitroparatolylthiocarbimide.** By H. STEUDEMANN (*Ber.*, 16, 2336—2338).—Neither of the isomerides of metanitraniline appear to form isomerides of metanitrophenylthiocarbimide; and of its homologues, orthonitroparatoluidine alone yields a thiocarbimide.

*Orthonitroparatolylphenylthiocarbimide*,  $\text{NO}_2.\text{MeC}_6\text{H}_3.\text{NH}.\text{CS}.\text{NHPh}$ , is obtained by acting on an alcoholic solution of orthonitroparatoluidine with phenylthiocarbimide; it melts at  $143^\circ$ , and is easily soluble in alcohol and glacial acetic acid. It is isomeric with the nitrophenylparatolylthiocarbimide melting at  $173^\circ$ , described in the preceding Abstract.

*Orthonitroparatolylthiocarbimide*,  $\text{CSN}.\text{C}_6\text{H}_3\text{Me}.\text{NO}_2$ , obtained by boiling the solution of the above compound in acetic anhydride with water; phenylthiocarbimide, acetanilide, and nitro-acetotoluide are amongst the products of this reaction. It crystallises in broad needles, which melt at  $56-57^\circ$ , and resemble metanitrophenylthiocarbimide in its properties. When heated with water, it forms hydric sulphide, carbonic anhydride, and *dinitrodiparatolylthiocarbimide*,  $\text{CS}[\text{NH}.\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2]_2$ , which is also obtained by acting on nitrotoluidine with nitrotolylthiocarbimide. It melts at  $207^\circ$ , is soluble in glacial acetic acid, and when heated with acetic anhydride is resolved into orthonitroparatolylthiocarbimide and nitroacetotoluide.

*Orthonitroparatolylethylthiourethane*,  $\text{EtO}.\text{CS}.\text{NH}.\text{C}_6\text{H}_3\text{Me}.\text{NO}_2$ , formed by slow decomposition of the alcoholic solution of orthonitroparatolylthiocarbimide, melts at  $95.5^\circ$ .

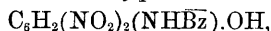
*Orthonitromonoparatolylthiocarbimide*,  $\text{NH}_2.\text{CS}.\text{NHC}_6\text{H}_3\text{Me}.\text{NO}_2$ , obtained by dissolving the thiocarbimide in ammonia, forms a citron-yellow powder melting at  $176^\circ$ .

*Orthonitrodiparatolylthiocarbamide,*

formed by mixing alcoholic solution of paratoluidine and nitrotolylthiocarbimide, crystallises from alcohol in needle-shaped crystals melting at 169°.

P. P. B.

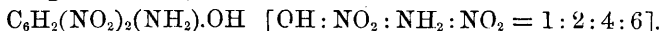
**An Isopicramic Acid.** By C. W. DABNEY (*Amer. Chem. J.*, 5, 20—30).—*α-Benzoylamidosalicylic acid*,  $\text{C}_6\text{H}_5(\text{NH}\bar{\text{Bz}})(\text{OH})\cdot\text{COOH}$ , is obtained, together with two other substances not yet fully investigated, by the action of benzoic chloride on *α*-metamidosalicylic acid. It forms a white powder, melts at 252°, is readily soluble in acetic acid, sparingly in hot water, insoluble in chloroform, benzene, and light petroleum. The barium salt,  $(\text{C}_{14}\text{H}_{10}\text{O}_4\text{N})_2\text{Ba} + 6\text{H}_2\text{O}$ , forms small colourless needles readily soluble in water. The calcium salt,  $(\text{C}_{14}\text{H}_{10}\text{O}_4\text{N})_2\text{Ca}$ , forms little blunt needles of satiny lustre. The nitration of the acid was accompanied with some difficulty, pure nitric acid acting on it with ungovernable violence; finally, by dissolving the substance in 20—30 times its weight of acetic acid, adding five drops of nitric acid to each 100 c.c. of liquid, and heating to 80°, the nitration was effected. The resulting compound was, however, not the nitro-acid expected, but *benzoylparamidodinitrophenol*,



small quantities of benzoic acid and picric acid being also formed. It crystallises in glistening yellow plates, gives off red vapours at 150°, and then melts at 250°. It is readily soluble in glacial acetic acid, somewhat less in alcohol, benzene, and naphtha, sparingly soluble in water. It acts as a strong acid, forming salts which crystallise well, and yield deep bluish-red solutions. The *potassium* salt,



forms light red needles with a splendid golden-yellow lustre; the anhydrous salt is of a dark brick-red colour. The *barium* salt,  $(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_6)_2\text{Ba} + 3\text{H}_2\text{O}$ , crystallises in slender bright red needles. The *calcium* salt,  $(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_6)_2\text{Ca} + 4\frac{1}{2}\text{H}_2\text{O}$ , crystallises in glistening yellowish-red scales or plates. The *lead* salt,  $(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_6)_2\text{Pb}$ , is obtained by precipitation as a dark red crystalline mass. When heated with moderately dilute hydrochloric acid at 130° for 12 hours, benzoylparamidodinitrophenol is resolved into benzoic acid and *diorthonitroparamidophenol* or *isopicramic acid*,



This crystallises in dark brown plates or needles, melts apparently with some decomposition at 170°, is sparingly soluble in cold water, soluble in benzene and naphtha, readily soluble in hot water or in alcohol; the solutions have a cherry-red colour. It appears to combine with acids, dissolving in them to form yellow solutions, but the compounds so formed could not be isolated. It unites with alkalis, forming crystalline salts, whose solutions are of a deep bluish-red colour. The *potassium* salt,  $\text{C}_6\text{H}_2(\text{NO}_2)_2(\text{NH}_2)\cdot\text{OK}$ , crystallises in bluish-black needles, and is very soluble in water. Both acid and

salts explode when heated. The properties of isopicramic acid and its derivatives are compared with those of picramic acid in the following table :—

*Picramic Acid*  $[\text{OH} : \text{NH}_2 : \text{NO}_2 : \text{NO}_2 = 1 : 2 : 4 : 6]$ , m. p.  $165^\circ$ .—Crystallises from water in orange-red needles, from chloroform in blood-red scales. Soluble in alcohol. 100 parts water at  $22^\circ$  dissolve 0.14 part acid; solubility in hot water about the same. Solutions orange-red in colour.

*Potassium Salt*.—Red translucent rhombic tables.

*Benzoylpicramic Acid*, m. p.  $220^\circ$ .—Greenish-yellow needles sparingly soluble in alcohol.

*Isopicramic Acid*  $[\text{OH} : \text{NO}_2 : \text{NH}_2 : \text{NO}_2 = 1 : 2 : 4 : 6]$ , m. p.  $170^\circ$ .—Crystallises in bundles of fine brownish-yellow needles, having a golden lustre when moist, very readily soluble in alcohol. 100 parts water at  $22^\circ$  dissolve 0.082 of acid; at just below the boiling point 0.812 part of acid. Solutions bluish red.

*Potassium Salt*.—Bluish-black needles.

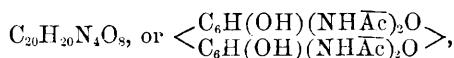
*Benzoylisopicramic Acid*, m. p.  $250^\circ$ .—Reddish plates of golden lustre, soluble in alcohol.

A. J. G.

*Note*.—Another isomeride of picramic acid,  $\beta$ -dinitroamidophenol, of unknown constitution, has been prepared by Henriques (Abstr., 1883, 328) by the action of ammonia on the trinitrophenols from  $\delta$ -dinitrophenol. It crystallises in brilliant red needles, melts at  $202^\circ$ , is nearly insoluble in water, sparingly soluble in alcohol, and yields a potassium salt crystallising in yellow needles.—A. J. G.

**Triamidophenol.** By E. BAMBERGER (*Ber.*, 16, 2400—2403).—Triamidophenol hydrochloride was prepared by reducing picric acid with tin and hydrochloric acid and precipitating the tin from the product with zinc. The hydrochloride so prepared was next converted into the *triacetyl-triamidophenol*,  $\text{C}_6\text{H}_2(\text{NH}\overline{\text{Ac}})_3\text{OH}$ , by heating it with acetic anhydride and sodium acetate. This compound crystallises from water in white leaflets melting at  $263^\circ$ . It is sparingly soluble in benzene and acetone, but more easily in alcohol, water, or glacial acetic acid. It is easily soluble in alkalis and ammonia, and is precipitated from these solutions by acids.

It was next attempted to nitrate this acetyl compound, with the result, however, of producing the quinone,



which is also produced when the acetyl compound is treated with weak oxidising agents such as dilute nitric acid or ferric chloride. This quinone crystallises from glacial acetic acid in golden-yellow leaflets melting at  $268^\circ$ , sparingly soluble in alcohol and water.

The corresponding quinol, viz., tetracetamidodihydroxyphenyl quinol,  $[\text{C}_6\text{H}(\text{OH})_2(\text{NH}\overline{\text{Ac}})_2]_2$ , is obtained by treating the quinone suspended in water with hydrogen sulphide. It crystallises from alcohol in colourless needles.

P. P. B.

**Condensation Products of Paranitrobenzyl Alcohol.** By A. BASLER (*Ber.*, **16**, 2714—2720).—The nitrobenzyl alcohol used in these experiments was prepared from paranitrocinnamic acid. The best results are obtained by dissolving 103.5 grams of methyl nitrocinnamate in 1400 grams of sulphuric acid, and gradually adding 135.5 grams of potassium nitrate to the solution, which must be kept at a temperature between 60° and 70°. When the reaction is complete, the mixture is left at rest for six hours, and afterwards poured into 10 times its volume of ice water. The precipitate is treated with a 3 per cent. solution of sodium carbonate, washed, and recrystallised from hot water. To convert the nitrobenzaldehyde into the alcohol, one part of the powdered aldehyde is dissolved in 5—6 parts of 15 per cent. soda solution. After 12 hours, the solid product is dissolved in a small quantity of water and extracted with ether. The alcohol is deposited from the ethereal solution in crystals melting at 92°. From 80 to 90 per cent. of the aldehyde is converted into alcohol. Nitrobenzyl alcohol was also prepared from the acetate. The yield is about 75 per cent. of the theoretical.

When a solution of nitrobenzyl alcohol in benzene is treated with strong sulphuric acid, two condensation products are formed. The one, *dinitrodibenzylbenzene*  $[C_6H_4(NO_2)_2CH_2]_2C_6H_5$ , is sparingly soluble in the usual solvents with the exception of benzene, in which it is tolerably soluble. It forms needle-shaped crystals which soften at 140° and melt at 146°. The other, *para-mononitrodiphenylmethane*,  $C_6H_4(NO_2).CH_2Ph$ , melting at 31°, is freely soluble in benzene, ether, and alcohol. It is deposited from the alcoholic solution in prisms. Chromic acid converts monodiphenylmethane, in acetic acid solution, into *para-mononitrobenzophenone*,  $C_6H_4(NO_2)CO.Ph$ , melting at 138°. It is freely soluble in benzene, in hot water, and in boiling alcohol. On reduction with tin and hydrochloric acid, mononitrodiphenylmethane is converted into *monamidodiphenylmethane*. This base forms white crystals melting at 34°, which rapidly change on exposure to the air. The sulphate, hydrochloride, and zinc chloride are crystalline salts. By means of the diazo-reaction it can be converted into *para-monhydroxydiphenylmethane*,  $C_6H_4(OH).CH_2Ph$ , which is identical with the compound Paternò obtained by the action of zinc-dust on phenol and benzyl chloride (*Ber.*, **5**, 288, 435; **15**, 153).

By dissolving *para-mononitrodiphenylmethane* in fuming nitric acid, a *dinitrodiphenylmethane* is obtained which melts at 175°. It has a musk-like odour, and is perhaps identical with Doer's isodinitrodiphenylmethane (*Ber.*, **5**, 795).

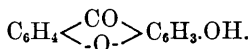
W. C. W.

**Action of Aromatic Hydroxy-acids on Phenols.** By A. MICHAEL (*Amer. Chem. J.*, **5**, 81—97).—Phenol and salicylic acid do not react on each other when heated either in open vessels or sealed tubes, but on addition of dehydrating agents, best stannic chloride, a reaction is readily effected, the products being paradihydroxybenzophenone and a new substance, salicylphenol, the former appearing to owe its formation to parahydroxybenzoic acid contained in the salicylic acid used.

*Salicylphenol*,  $\text{C}_6\text{H}_4(\text{OH})\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , crystallises from hot water or alcohol in pale yellow plates, from benzene in pyramids with symmetrically truncated end-faces. It melts at  $143\text{--}144^\circ$ , is nearly insoluble in cold, moderately soluble in hot water, readily soluble in alcohol and benzene. It dissolves readily in alkalis, yielding metallic derivatives. The *sodium* compound,  $\text{C}_{13}\text{H}_8\text{O}(\text{ONa})_2$ , forms stellate groups of needles, very soluble in water and alcohol; the *silver* compound,  $\text{C}_{13}\text{H}_8\text{O}(\text{OAg})_2 + \text{H}_2\text{O}$ , is obtained as a bright yellow precipitate, sparingly soluble in water. The mercury compound forms reddish-yellow needles, the ferric salt is obtained in brown fern-shaped crystals, the copper salt crystallises in groups of greenish-yellow rhombic plates, the lead salt was obtained as an amorphous yellow precipitate which melts in boiling water. *Diacetylsalicylphenol*,  $\text{C}_{13}\text{H}_8\text{O}(\text{OAc})_2$ , prepared by heating a mixture of salicylphenol, acetic anhydride, and sodium acetate, crystallises in long concentrically grouped white needles, melts at  $84\text{--}85^\circ$ , is sparingly soluble in cold, moderately soluble in hot water, readily soluble in hot alcohol or benzene. From its formation from salicylic acid, one hydroxyl-group in salicylphenol must be in the ortho-position to the carbonyl-group, and as parahydroxybenzoic acid occurs largely amongst the products of its decomposition by fusion with sodium or potassium hydroxides, it is most probable that the second hydroxyl-group is in the para-position.

*Ortho-para-dihydroxydiphenylcarbinol*,  $\text{C}_6\text{H}_4(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , is obtained by the action of sodium-amalgam on an alkaline solution of salicylphenol, and is precipitated on saturating the liquid with carbonic anhydride, as a white amorphous powder which could not be crystallised. It becomes strongly electric on rubbing, is insoluble in cold, sparingly soluble in hot water, readily soluble in cold alcohol, the solution, on evaporation, yielding an oil that does not solidify on standing. It dissolves readily in alkalis, yielding metallic derivatives. Like the corresponding dipara-compound (*Annalen*, **202**, 132) it gives an intense violet-blue coloration when heated with mineral acids.

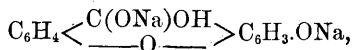
*Salicylresorcinol*,  $\text{C}_6\text{H}_4(\text{OH})\text{CO}\cdot\text{C}_6\text{H}_3(\text{OH})_2$ , is obtained in small quantity, by heating a mixture of salicylic acid and resorcinol at  $195\text{--}200^\circ$  for 15 hours. It crystallises from alcohol in glittering yellow scales, melts at  $133\text{--}134^\circ$ , and resolidifies at  $116\text{--}117^\circ$ ; it volatilises slowly in a current of steam. It is insoluble in cold, sparingly soluble in hot water, readily soluble in alcohol, benzene, or in alkalis. Acetic anhydride converts it into an acetyl-derivative; an oil which solidifies partially on long standing. Reduction with sodium-amalgam gives a substance resembling the dihydroxydiphenylcarbinols. In presence of dehydrating agents (best zinc chloride) the reaction between salicylic acid and resorcinol takes rather a different course, the product of the action being *salicylresorcinol ether*,



This compound crystallises in long bright yellow needles, melts at



146—147°, is insoluble in cold, sparingly soluble in hot water. It is also formed by the action of zinc chloride on salicylresorcinol. Fused with alkalis, it yields salicylic acid and resorcinol. Its metallic derivatives are characterised by their insolubility in water. A *sodium* compound,  $C_{13}H_7O_3Na.NaOH$ , is obtained by the action of sodium methylate on the ether. It crystallises in long lemon-yellow needles, and on long washing with cold water is completely decomposed into sodium hydroxide and salicylresorcinol ether. A mono-sodium-derivative could not be obtained in a state of purity. The author considers it very probable that the disodium-derivative has the composition



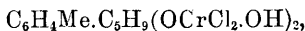
as from its behaviour with water it must be regarded as a derivative of the ether and not of salicylresorcinol. *Acetylsalicylresorcinol ether*,  $C_6H_4 < \begin{array}{c} CO \\ \text{---} O \text{---} \end{array} > C_6H_3.O\overline{Ac}$ , crystallises in white prismatic needles, melts at 167—168°, is sparingly soluble in water, readily soluble in hot alcohol.

*Salicylorcinol ether*,  $C_6H_4 < \begin{array}{c} O \\ \text{---} CO \end{array} > C_6H_2.Me.OH$ , is prepared by heating a mixture of salicylic acid, orcinol, and zinc chloride. It crystallises in straw-coloured silky needles, melts at 140°, is insoluble in water, soluble in hot alcohol. Fused with alkalis, it yields salicylic acid and orcinol. The *sodium* derivative,  $C_{11}O_3H_9Na + 1\frac{1}{2}H_2O$ , crystallises in long yellow needles; a disodium-compound could not be obtained. *Acetylsalicylorcinol ether*,  $C_{14}H_9O_3\overline{Ac}$ , crystallises in long needles, and melts at 151—152°. A. J. G.

**Conversion of Hydrocarbons into Aldehydes by the Action of Chromyl Dichloride.** By A. ÉTARD (*Compt. rend.*, 97, 909—911).—The author repeats, in reply to Paternò and Scichilone, that pure cumene yields cumaldehyde when the compound which it forms with chromyl dichloride is decomposed by water.

When a 10 per cent. solution of mesitylene in carbon bisulphide is mixed with a similar solution of chromyl dichloride, a precipitate is obtained of the composition  $C_6H_3Me_2.CH(OCrCl_2.OH)_2$ , and when this is decomposed by water it yields mesitylaldehyde in almost theoretical quantity. It boils at 220—222°, and oxidises rapidly on exposure to air, yielding mesitylenic acid.

Amyl-toluene, boiling at 213—218°, when treated in a similar manner at 45°, yields a precipitate of the composition



and when this is decomposed by water, a mixture of two isomeric aldehydes of the composition  $C_{12}H_{16}O$  is obtained.

Phenetoil, in the same manner, yields a substance  $C_8H_6O_4$ ; ortho-cresol yields  $C_7H_6O_3$ ; and paracresol,  $C_{14}H_{10}O_3$ . These substances apparently resemble the quinones in character. They dissolve in alkalis, but are insoluble in acids. Styrolene also forms a definite compound with chromyl dichloride, but it has not yet been examined.

C. H. B.

**Action of Benzaldehyde on the Mononitro-derivatives of the Paraffins.** By B. PRIEBES (*Ber.*, 16, 2591).—When nitromethane and benzaldehyde in molecular proportions are heated with zinc chloride in a sealed tube at 160°, phenylnitroethylene,  $\text{CHPh}:\text{CH}.\text{NO}_2$ , melting at 56·5—57°, is produced:  $\text{Ph}.\text{COH} + \text{CH}_3.\text{NO}_2 = \text{H}_2\text{O} + \text{CHPh}:\text{CH}.\text{NO}_2$ . In the same way nitroethane and benzaldehyde yield a phenylnitropropylene,  $\text{CHPh}:\text{CMe}.\text{NO}_2$ , melting at 64°.

A. K. M.

**Ammonia-derivatives of Benzil.** (Preliminary Notice.) By F. R. JAPP (*Ber.*, 16, 2636—2640).—According to Zincke and Henius, (*Ber.*, 16, 889) the compounds *imabenzil*, *benzilimide*, and *benzilam*, obtained by Laurent, have the formulæ  $\text{C}_{42}\text{H}_{32}\text{N}_2\text{O}_4$ ,  $\text{C}_{42}\text{H}_{32}\text{N}_2\text{O}_4$ , and  $\text{C}_{42}\text{H}_{32}\text{N}_2\text{O}_2$  respectively. The author refers to previous communications (this Journal, Trans., 1883, p. 12, and *Ber.*, 15, 2413), in which he has shown that the formula of azobenzil (benzilam) is  $\text{C}_{21}\text{H}_{15}\text{NO}$ , and not  $\text{C}_{42}\text{H}_{30}\text{N}_2\text{O}_2$ , as Zinin assumed (*Annalen*, 34, 190). Its vapour-density also excludes the formula proposed by Zincke and Henius. When heated with concentrated hydrochloric acid at 250°, it yields benzoic acid, ammonium chloride, and a resinous mass. If oxidised by chromic mixture, benzoic acid is obtained in almost the theoretical amount required by the equation  $\text{C}_{21}\text{H}_{15}\text{NO} + \text{O}_2 + 3\text{H}_2\text{O} = 3\text{C}_7\text{H}_6\text{O}_2 + \text{NH}_3$ , showing that three benzenyl groups must be present in the compound. Moreover, azobenzil is closely analogous in its behaviour to benzenylamidophenanthrol, the constitution of which is known. These facts leave little doubt as to the correctness of the constitutional formula previously assumed by the author (*loc. cit.*). According to Zincke, the conversion of *benzilimide* into azobenzil by cold concentrated sulphuric acid, consists in the removal of oxygen, and as the latter does not appear in the free state it must be assumed to oxidise a part of the substance. This, however, is not in accordance with the fact that the change is very complete, and the author thinks it far more probable that water is eliminated, which might occur in the following manner, if benzilimide be assumed to have the formula  $\text{C}_{21}\text{H}_{17}\text{NO}_2$ , thus:  $\text{C}_{21}\text{H}_{17}\text{NO}_2 - \text{H}_2\text{O} = \text{C}_{21}\text{H}_{15}\text{NO}$ . This formula also agrees better with the results of analysis than that given by Zincke.

The constitution, 
$$\begin{array}{c} \text{PhC}-\text{O} \\ \parallel \\ \text{PhC}.\text{NH} \end{array} \rangle \text{C}(\text{OH})\text{Ph}$$
, is suggested, according to

which benzilimide would also be a condensation-product of benzaldehyde and benzil with ammonia. The author agrees with Zincke that *imabenzil* has the formula  $\text{C}_{42}\text{H}_{32}\text{N}_2\text{O}_4$ ; the halved formula would require that half the benzil taking part in the reaction should be decomposed, but the yield of imabenzil is too great for this. Moreover, on boiling it with dilute sulphuric acid, almost exactly the same weight of benzil is obtained:  $\text{C}_{42}\text{H}_{32}\text{N}_2\text{O}_4 + 2\text{H}_2\text{O} = 3\text{C}_{14}\text{H}_{10}\text{O}_2 + 2\text{NH}_3$ , this being the reverse of Zincke's method of forming it. Imabenzil contains therefore neither benzoic acid nor benzaldehyde radicals, and must be derived from 3 mols. of benzil.

A. K. M.

**Action of Nitriles on Benzil.** By F. R. JAPP and R. C. TRESIDDER (*Ber.*, 16, 2652—2654).—On adding acetaldehyde and

benzonitrile to well cooled concentrated sulphuric acid, Hepp and Spiess obtained a compound of the formula  $C_{16}H_{15}N_2O_2$ ;  $C_2H_5O + 2C_7H_5N + H_2O = C_{16}H_{15}N_2O_2$ . The authors find that a similar reaction takes place with benzil and propionitrile. Finely powdered benzil is suspended in four times its weight of concentrated sulphuric acid, and propionitril gradually added, the mixture being agitated and cooled. After remaining at rest for some hours, it is poured into water and the white product washed with ether and crystallised from boiling alcohol. It forms lustrous colourless needles of the formula  $C_{20}H_{22}N_2O_3$ , melting at  $197^\circ$ :  $C_{14}H_{10}O_2 + 2C_3H_5N + H_2O = C_{20}H_{22}N_2O_3$ . On boiling it with dilute sulphuric acid, it yields benzil, propionic acid, and ammonia:  $C_{20}H_{22}N_2O_3 + 3H_2O = C_{14}H_{10}O_2 + 2C_2H_5COOH + 2NH_3$ . When benzil and benzonitril are treated as above described, the product consists of two compounds, which can be separated by crystallisation from alcohol. The more soluble compound forms colourless prisms melting at  $168^\circ$ , which crystallise with half a molecule of alcohol,  $2C_{28}H_{21}N_2O_3 + C_2H_5O : C_{14}H_{10}O_2 + 2C_7H_5N + H_2O = C_{28}H_{21}N_2O_3$ . The second substance,  $C_{28}H_{21}NO_3$ , is nearly insoluble in alcohol and in most of the usual solvents, but can be purified by crystallisation from boiling benzene, when it is obtained in microscopic prisms melting at  $225^\circ$ . Its formation probably takes place thus:  $2C_{14}H_{10}O_2 + C_7H_5N + H_2O = C_{28}H_{21}NO_3 + PhCOOH$ . When it is heated with concentrated hydrochloric acid at  $150^\circ$ , it is decomposed, benzil, benzoic acid, and ammonia being formed, probably according to the equation  $C_{28}H_{21}NO_3 + 2H_2O = C_{14}H_{10}O_2 + C_7H_5O_2 + C_7H_5O + NH_3$ ; the authors did not succeed in confirming the formation of benzaldehyde. Acetic anhydride, at  $150^\circ$ , has no action on the substance. A. K. M.

**Substituted Benzoic Acids, and the Nature of the Hydrogen Atoms in Benzene.** Part I. By H. HÜBNER (*Annalen*, 222, 67—115).—I. Metanitrobenzoic acid melting at  $142^\circ$  is prepared by adding finely powdered benzoic acid to nitric acid (sp. gr. 1.5), and then boiling for 24 hours. It is separated from the orthonitrobenzoic acid simultaneously formed, by means of the sodium salt, which is more soluble in the case of the ortho-acid. The preparation of dimetanitrobenzoic acid melting at  $205^\circ$ , by the action of a mixture of strong sulphuric and fuming nitric acids on benzoic acids, has been already described (Abstr., 1878, 148). The same acid may also be obtained from the above metanitrobenzoic acid by the action of a mixture of strong sulphuric and nitric acids. The preparation of the same dinitro-acid from paratoluidine was made known by W. Staedel (Abstr., 1881, 724). Paraorthonitrobenzoic acid,



is prepared by heating paranitrobenzoic acid with a mixture of equal volumes of the strongest nitric and commercial sulphuric acids at  $170^\circ$ . The acid is purified by means of its barium and lead salts: it melts at  $179^\circ$ . This nitration has since been studied by Claus and Halberstadt (Abstr., 1880, 647), who find that a second dinitrobenzoic acid is simultaneously formed. From the above it

appears that the  $\text{NO}_2$ -group in entering into mononitrobenzene-derivatives principally replaces those hydrogen atoms which are in the meta-position, irrespectively of any oxatyl-, methyl-, or amido-groups, which may be already present in the molecule.

II. The preparation of metanitrometamidobenzoic acid melting at  $208^\circ$  has been already described (Abstr., 1878, 148). Metamidobenzoic acid is prepared by passing sulphuretted hydrogen through an ammoniacal solution of metadinitrobenzoic acid until the solution yields no precipitate with hydrochloric acid. The acid crystallises with 1 mol.  $\text{H}_2\text{O}$ , and melts at  $228^\circ$ . By heating the dry hydrochloride of this acid with barium hydroxide, dimetamidobenzene melting at  $60^\circ$  is obtained. This shows that the dinitrobenzoic acid melting at  $204^\circ$ , which is the chief product of the nitration of monometanitrobenzoic acid, has the two nitro-groups in the meta-position relatively to each other.

The nitramidobenzoic acid melting at  $208^\circ$  was converted by means of the diazo-compound into metanitrobenzoic acid melting at  $142^\circ$ , and this again, by means of tin and hydrochloric acid, into metamidobenzoic acid melting at  $172.5^\circ$ . The same metanitramidobenzoic acid melting at  $208^\circ$  was converted by means of the diazo-compound into metanitrochlorobenzoic acid melting at  $147^\circ$ ; then, by means of zinc and hydrochloric acid, the latter was converted into metamidochlorobenzoic acid melting at  $216^\circ$ , and this again, through the diazo-compound, into metachlorobenzoic acid melting at  $153^\circ$ . Thus both the nitro-groups in the dinitrobenzoic acid are shown to be in the meta-position. These experiments and results may be thus briefly tabulated:—

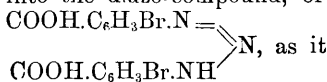
		[1	:	3	:	5.]
Dimetanitrobenzoic acid....		$\text{COOH}$		$\alpha\text{NO}_2$		$\beta\text{NO}_2$
Metranitramidobenzoic „ ....		$\text{COOH}$		$\alpha\text{NO}_2$		$\beta\text{NH}_2$
Metanitrobenzoic „ ....		$\text{COOH}$		$\alpha\text{NO}_2$		H
$\alpha$ -Metachlorobenzoic „ ....		$\text{COOH}$		$\alpha\text{Cl}$		H
Metanitrochlorobenzoic „ ....		$\text{COOH}$		$\alpha\text{NO}_2$		$\beta\text{Cl}$
Metamidochlorobenzoic „ ....		$\text{COOH}$		$\alpha\text{NH}_2$		$\beta\text{Cl}$
$\alpha\beta$ -Metachlorobenzoic „ ....		$\text{COOH}$		H		$\beta\text{Cl}$

III. When metachlorobenzoic acid is acted on by fuming nitric acid, two nitrochlorobenzoic acids are produced. As it may be assumed that the nitric acid acts in the same way as on metabromobenzoic acid, the two acids must be metachlororthonitrobenzoic acids. The two acids are separated by repeatedly boiling them with small quantities of water until the undissolved portion ( $\alpha$ -metachloronitrobenzoic acid melting at  $235^\circ$ ) no longer melts under water. The solution contains the  $\beta$ -metachloronitrobenzoic acid melting at  $137^\circ$ . The properties, both of the acids themselves and of their respective salts, are quite distinct, thus demonstrating that in monosubstituted benzenes there are two atoms of hydrogen in the ortho-position.

IV. Hitherto for the preparation of  $\alpha$ - and  $\beta$ -orthonitrometabromobenzoic acid, purified bromobenzoic acid from bromine and benzoic acid has been employed (*Ber.*, 8, 558; Abstr., 1878, 148).

Owing to the difficulty of separating the products of such an action as that of bromine on benzoic acid, the suspicion might arise that these isomeric bromonitrobenzoic acids had been formed from different bromobenzoic acids. In order to obviate this objection, pure metanitrobenzoic acid was converted into metamido-, and then into metabromobenzoic acid, and this on treatment with nitric acid yielded the  $\alpha$ - and  $\beta$ -orthonitrometabromobenzoic acids as with the ordinary bromobenzoic acid. To prepare the  $\alpha$ -orthobromometabromobenzoic acid, the above  $\alpha$ -orthonitro-acid was converted into the diazo-compound, or

rather into the diazoimido-compound,



proved to be, and the latter into the dibromobenzoic acid, which melts at  $147^\circ$ .

To prepare the metabromo- $\beta$ -orthobromobenzoic acid, the above  $\beta$ -orthonitro-acid was first converted into the metabromo- $\beta$ -orthamido-benzoic acid. The further conversion of the latter, by means of the diazo-compound, into dibromobenzoic acid, is attended with much difficulty. The hydrobromide of the amido-acid is first prepared, treated with nitrous anhydride in the cold, and finally boiled. The metabromo- $\beta$ -orthobromobenzoic acid melts at  $153^\circ$ .

The two isomeric bromamidobenzoic acids were also converted into amidobenzoic acid by means of sodium-amalgam. In both cases, the same amidobenzoic acid melting at  $144^\circ$ , and identical with anthranilic acid or orthamidobenzoic acid was obtained, thus confirming the already demonstrated existence of two ortho-hydrogen atoms in mono-substituted benzene.

That the existence of two isomeric metabromorthonitrobenzoic acids depends on the different relationship between the bromine- and nitro-groups, was shown by converting these acids into dibromobenzene. The  $\beta$ -compound was found to yield paradibromo-, and the  $\alpha$ -compound orthodibromobenzene, thus:—

Metabromo- $\beta$ -orthonitrobenzoic acid.  
[COOH : NO<sub>2</sub> : Br = 1 : 2 : 5].

Metabromo- $\alpha$ -orthonitrobenzoic acid.  
[COOH : NO<sub>2</sub> : Br = 1 : 2 : 3].

Metabromo- $\beta$ -orthobromobenzoic acid.  
[COOH : Br : Br = 1 : 2 : 5].

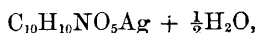
Metabromo- $\alpha$ -orthobromobenzoic acid.  
[COOH : Br : Br = 1 : 2 : 3].

Paradibromobenzene.  
[Br : Br = 2 : 5].

Orthodibromobenzene.  
[Br : Br = 2 : 3].

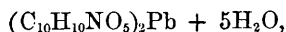
P. F. F.

**Nitrohydroxypropylbenzoic Acid and its Derivatives.** By O. WIDMANN (*Ber.*, 16, 2567—2575).—This acid, together with some of its derivatives, have been already described by the author (*Abstr.*, 1883, 330). The *ammonium salt*,  $\text{C}_{10}\text{H}_{10}\text{NO}_5\text{NH}_4 + 2\text{H}_2\text{O}$ , forms lustrous needles extremely soluble in water; the *silver salt*,



separates from a warm solution in needles, and from a cold solution in well-formed prisms or rhombic plates, sparingly soluble in cold, more

readily in warm water; the *calcium salt*,  $(C_{10}H_{10}NO_5)_2Ca$ , crystallises in sparingly soluble white needles, the *barium salt*,  $(C_{10}H_{10}NO_5)_2Ba + 6H_2O$ , in highly lustrous needles, 1 part of the latter salt (anhydrous) dissolving in 11 parts water at  $13^\circ$ . The *lead salt*,



forms short lustrous prisms very sparingly soluble in water, and the *copper salt*,  $(C_{10}H_{10}NO_5)_2Cu + 1\frac{1}{2}H_2O$ , bluish-green prismatic or cubical crystals, also very sparingly soluble in water, although readily in alcohol, from which it crystallises in small green slender needles. *Nitroacetoxypropylbenzoic acid*,  $C_6H_3(NO_2)(CMe_2.OAc).COOH$ , is obtained when nitrohydroxypropylbenzoic acid is heated with an excess of acetic anhydride in sealed tubes at  $100^\circ$ , the solution repeatedly evaporated with alcohol, and the oily product crystallised from a mixture of ether with a little alcohol. It forms colourless rhomboidal pyramids melting at  $131-133^\circ$ , and extremely readily soluble in alcohol, ether, and the usual solvents, almost insoluble in water.

*Salts of Nitropropenylbenzoic Acid*.—The *ammonium salt* is extremely soluble in water, and crystallises at ordinary temperatures in white needles,  $C_{10}H_8NO_4.NH_4$ ; the *silver salt*,  $C_{10}H_8NO_4Ag$ , forms clusters of white needles, or on rapidly cooling its hot solution, slender white feathery needles, very sparingly soluble in cold, more readily in warm water; the *calcium salt*,  $(C_{10}H_8NO_4)_2Ca + 2H_2O$ , separates in clusters of slender white needles, very sparingly soluble in water; the *barium salt*,  $(C_{10}H_8NO_4)_2Ba + 3\frac{1}{2}H_2O$ , crystallises in small white concentrically grouped needles, very sparingly soluble in cold, much more readily in warm water; the *copper salt*,  $(C_{10}H_8NO_4)_2Cu + H_2O$ , obtained by precipitating the ammonium salt with copper sulphate, forms a bluish-green precipitate; it begins to decompose above  $100^\circ$ , whilst long white needles sublime, insoluble in water, readily soluble in potash, and melting at about  $150^\circ$ . *Amidohydroxypropylbenzoic acid*,  $C_6H_3(NH_2)(CMe_2.OH).COOH$ , is prepared by dissolving the nitro-acid (5 grams) in an excess of ammonia, and gradually adding a solution of ferrous sulphate (40 grams). The mixture is supersaturated with ammonia, warmed on a water-bath, and the nearly colourless filtrate treated with acetic acid and repeatedly extracted with ether, from which, after purification, the amido-acid crystallises in colourless lustrous prisms, which do not melt at  $270^\circ$ . It is almost insoluble in benzene, readily soluble in alcohol, very sparingly in ether, and moderately soluble in water; it possesses very feeble acid as well as basic properties; it yields amidopropenylbenzoic acid when boiled with hydrochloric acid.

*Acetamidohydroxypropylbenzoic acid*,  $N\bar{A}cH.C_6H_3(CMe_2.OH).COOH$ , is obtained by the action of acetic anhydride (1 mol.) on amidohydroxypropylbenzoic acid (1 mol.), the two substances reacting violently with great evolution of heat, the product soon solidifying to a hard brittle mass. It is very sparingly soluble in boiling alcohol, from which it separates as a white crystalline powder, which does not melt at  $280^\circ$ . *Amidopropenylbenzoic acid*,  $NH_2.C_6H_3(C_3H_5).COOH$ , is prepared from the corresponding nitro-compound by reduction with

ammonia and ferrous sulphate. It crystallises in long white lustrous needles melting at 93–94°, and is readily soluble in ether, alcohol, chloroform, and benzene, sparingly in light petroleum and in water. It may also be obtained by boiling amidohydroxypropylbenzoic acid with hydrochloric acid. On evaporating the solution, the hydrochloride is obtained, and may be decomposed by sodium hydroxide, and the acid separated by the addition of acetic acid. The *hydrochloride*,  $\text{COOH.C}_6\text{H}_3(\text{C}_3\text{H}_5).\text{NH}_2\text{Cl}$ , crystallises in long colourless prisms, very readily soluble in water, and yields a readily soluble platinochloride. The *acetate*,  $\text{COOH.C}_6\text{H}_3(\text{C}_3\text{H}_5).\text{NH}_2.\text{AcOH}$ , crystallises in short colourless well-formed prisms, melting at about 160°, with evolution of gas and formation of a substance of very high melting point; this behaviour is due to the presence of water of crystallisation. Considerable evolution of heat takes place when acetic anhydride (1 mol.) acts on amidopropenylbenzoic acid, and *acetamidopropenylbenzoic acid*,  $\text{NAcH.C}_6\text{H}_3(\text{C}_3\text{H}_5).\text{COOH}$ , is formed. It crystallises from dilute alcohol in white flat needles melting at 210–212°. If an excess of acetic anhydride is used, the second amido-hydrogen seems to be replaced, the product melting at 215–216°. Acetamidopropenylbenzoic acid is sparingly soluble in boiling water, from which it crystallises in long needles; it is insoluble in cold, but soluble in boiling dilute sulphuric acid, from which it crystallises unchanged; it is also insoluble in cold hydrochloric acid, and on boiling dissolves with difficulty and with partial saponification and formation of the hydrochloride of a new compound (see p. 303).

A. K. M.

**Conversion of Active Mandelic Acid into Inactive.** By J. LEWKOWITSCH (*Ber.*, 16, 2721–2722).—When *lævomandelic acid* is heated at 160° in a sealed tube for 30 hours, it is converted into benzaldehyde and inactive mandelic acid. By means of the cinchonine salt, the inactive acid can be split up into the two optically active varieties. When *paramandelic acid* is exposed to the action of *schizomycetes*, the *dextromandelic acid* is decomposed, but the *lævoacid* remains.

W. C. W.

**Dipyrogallopropionic Acid.** By C. BÖTTINGER (*Ber.*, 16, 2404–2412).—By treating pyroracemic acid and pyrogallol with concentrated sulphuric acid, a mixture of this acid and its anhydride was obtained from which the former was separated by its greater solubility in water. The aqueous solutions, on spontaneous evaporation, leave a red resinous mass, which is easily soluble in glacial acetic acid, acetone, and alcohol. It is decomposed by heat, leaving the anhydride, and melts at 162°. The composition of this acid is expressed by the formula  $\text{C}_{15}\text{H}_{14}\text{O}_8$ . It dissolves in ammonia and alkalis, forming blue solutions, in which barium chloride, calcium chloride, and copper sulphate produce dark-blue precipitates.

*Methyl dipyrogallopropionate* is obtained by heating the acid with potash, methyl iodide, and methyl alcohol at 120°. It is a dark-brown powder melting below 100°.

Dipyrogallopropionic acid with acetic anhydride, yields a diacetyl-

derivative,  $C_{15}H_{10}Ac_2O_7$ ; this when treated with bromine yields a pentabromo-derivative,  $C_{15}H_5Br_5Ac_2O_7$ .

Dipyrogallopropionic acid treated with bromine in glacial acetic acid solution, yields a mixture of a tribromo- and pentabromo-derivative.

*Anhydrodipyrogallopropionic acid*,  $C_{15}H_{12}O_7$ , is obtained by heating the acid at  $100^\circ$ . It forms a reddish-brown powder soluble in hot water and dissolving in ammonia to a violet-coloured solution. When heated with acetic anhydride, it yields a diacetyl-derivative. Bromine reacts with a solution in glacial acetic acid or chloroform, forming a tribromo- and pentabromo-anhydropyrogallopropionic acid.

P. P. B.

**Properties of Ethylic Phenylsulphonacetates.** By A. MICHAEL and A. M. COMEY (*Amer. Chem. J.*, 5, 116—119).—*Ethylic phenylsulphonacetate*,  $PhSO_2.CH_2.COOEt$ , is obtained by the action of ethyl chloracetate on an alcoholic solution of sodium phenylsulphonate, the mixture being heated for 4—5 hours on the water-bath, the alcohol distilled off, the residue extracted with water, and the insoluble oil allowed to stand for some time, when it crystallises, and is purified by crystallisation from alcohol. Ethylic phenylsulphonacetate crystallises in clusters of long prisms, melts at  $45^\circ$ , is insoluble in water, sparingly soluble in cold, soluble in hot alcohol. Boiled with alkalis, it yields the metallic salts, which, on treatment with acids, give the free acid.

Sodium has little action on the ethyl salt; sodium ethylate, on the contrary, readily reacts, a mixture of the substances in molecular proportion dissolved in absolute alcohol soon solidifying to a mass of white needles of *ethyl sodium phenylsulphonacetate*,



This is sparingly soluble in cold, moderately soluble in hot alcohol, readily soluble in water; on acidifying, the original ether is precipitated.

*Ethylic benzylphenylsulphonacetate*,  $PhSO_2.CH(CH_2Ph).COOEt$ , is prepared by the action of benzyl chloride on the preceding compound; it forms short white prisms, melts at  $95$ — $96^\circ$ , is insoluble in water, readily soluble in hot alcohol. Heated with alcoholic sodium ethylate, it yields a sodium derivative which when treated with benzyl chloride gives the *dibenzyl derivative* melting at  $118^\circ$ . On heating the monobenzyl derivative with excess of alcoholic caustic soda in a closed tube at  $100^\circ$  for several hours, it yields cinnamic acid, according to the equation,  $C_6H_5.CH_2.CH(SO_2Ph).COOEt + 2KOH = C_6H_5.CH : CH.COOK + PhSO_2K + EtOH + OH_2$ .

These results show clearly that an acid radical such as  $PhSO_2$ , has as decided an effect as an acetyl-group in rendering the hydrogen of the  $CH_2$ -group to which it is attached sufficiently negative to be replaceable by metals.

A. J. G.

**Oxidation of Substitution-products of Aromatic Hydrocarbons. Experiments with Derivatives of Naphthalene.** By I. REMSEN and W. J. COMSTOCK (*Amer. Chem. J.*, 5, 106—111).—The



lead salts of  $\alpha$ - and  $\beta$ -naphthalenesulphonic acids were treated directly with phosphorous pentachloride and ammonia, and the amides so obtained submitted to oxidation. Satisfactory results were obtained only when potassium permanganate was employed as the oxidising agent. In neutral solution, or in alkaline solution with excess of permanganate, phthalic acid and sulphophthalic acid are obtained, whilst in alkaline solution with the permanganate not in excess of the amount theoretically required, sulphaminephthalic acids are obtained, together with a small quantity of phthalic acid.

$\alpha$ -Sulphophthalic acid could not be obtained pure in the free state; the barium salt,  $\left( \text{C}_6\text{H}_3 \begin{array}{c} \text{SO}_2 \\ \diagup \quad \diagdown \\ (\text{COO})_2 \end{array} \right) \text{Ba}_2 + 8\text{H}_2\text{O}$ , crystallises in aggregates of small clear and transparent plates. It loses 7 mols.  $\text{H}_2\text{O}$  below  $150^\circ$ . It is sparingly soluble in boiling water. The hydrous lead salt,  $\text{C}_6\text{H}_3(\text{COOH}) \begin{array}{c} \text{SO}_2\text{O} \\ \diagup \quad \diagdown \\ \text{COO} \end{array} \text{Pb} + \frac{1}{2}\text{H}_2\text{O}$ , crystallises in small prisms.

$\alpha$ -Sulphaminephthalic acid was not obtained free. Potassium  $\alpha$ -anhydrosulphaminephthalate,  $\text{C}_6\text{H}_3(\text{COOK}) \begin{array}{c} \text{SO}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{NH} + \text{H}_2\text{O}$ , crystallises in needles, is soluble in alcohol and water, insoluble in ether. Silver sulphaminephthalate,  $\text{C}_6\text{H}_3(\text{COOH})(\text{SO}_2\text{NH}_2).\text{COOAg}$ , forms colourless needles, is soluble in hot water, does not lose in weight at  $180^\circ$ , but appears to suffer decomposition when heated much at that temperature.

Dipotassium  $\beta$ -sulphophthalate,  $\text{C}_6\text{H}_3(\text{SO}_3\text{K})(\text{COOK}).\text{COOH} + 2\text{H}_2\text{O}$ , forms small prismatic crystals, readily soluble in water, nearly insoluble in alcohol. Potassium  $\beta$ -sulphaminephthalate,



crystallises in radiating groups of silky needles of a light straw colour, and is readily soluble in water. A. J. G.

**Aniluvitonic Acid.** By C. BÖTTINGER (*Ber.*, **16**, 2357—2359).—The hydrochloride of this acid suspended in chloroform and treated with bromine, forms a red oily liquid which, after being washed with chloroform and then with water, forms a reddish-yellow powder, losing bromine on exposure to the air. This same oily bromine addition-product is obtained by heating the hydrochloride with bromine in sealed tubes at  $120^\circ$ , but substitution-products are formed at the same time.

Aniluvitonic acid hydrobromide is obtained by spontaneous evaporation of its aqueous solutions in beautifully iridescent large prismatic tabular crystals, containing 2 mols.  $\text{H}_2\text{O}$ , whilst from hot saturated solutions it crystallises in long spikes containing  $\frac{1}{2}$  a mol.  $\text{H}_2\text{O}$ . Its aqueous solutions when not too dilute give a yellow precipitate with platinum chloride. When the hydrobromide is mixed with lime and distilled, it yields methylquinoline.

When the hydrochloride of aniluvitonic acid is heated with phthalic anhydride and zinc chloride, it gives a brownish-yellow colouring matter of a basic character, the hydrochloride of which reacts with methyl

iodide, yielding a brownish-red powder, which crystallises from alcohol and ether in yellow needles, and is probably a methylated derivative of aniluvitonic acid. P. P. B.

**Cymenesulphonic Acids.** By E. PATERNO (*Ber.*, 16, 2713).—A reply to Claus (*Ber.*, 16, 1297).

**“Oakbark Tannic Acid.”** By C. BÖTTINGER (*Ber.*, 16, 2710—2713).—In reply to Etti (*Abstr.*, 1883, 995), the author maintains that the tannic acid contained in oakbark must have the composition  $C_{19}H_{16}O_{10}$ , as it forms a bromine substitution-product,  $C_{19}H_{14}Br_2O_{10}$ , which yields a *pentacetic* derivative. Strong hydrochloric acid at  $200^\circ$  decomposes the dibromo-derivative into carbonic acid, water, and the compound  $C_{38}H_{18}O_{13}$ , from which a tetrabrominated derivative was obtained. The tannic acid contains 1 ketone oxygen-atom. When dibromotannic acid is acted on by bromine, 4 hydrogen-atoms are eliminated, but only two of them are replaced by bromine, and  $C_{19}H_{10}Br_4O_{10}$  is produced. This body also yields a pentacetic derivative.

Phlobaphen and “oak-red” have the composition  $C_{38}H_{26}O_{17}$ , five of the hydrogen-atoms being replaceable by acetyl. No methyl chloride is formed when the compound is converted into  $C_{36}H_{22}O_{11}$  by the action of hydrochloric acid at a high temperature. Phlobaphen yields two bromine derivatives,  $C_{38}H_{20}Br_2O_{17}$  sparingly soluble in alcohol, and  $C_{38}H_{16}Br_{10}O_{17}$  freely soluble in alcohol. Seven hydrogen-atoms in the first body can be replaced by acetyl.

Phlobaphen does not contain a ketone oxygen-atom. It is reduced by hydriodic acid, and yields ethers when treated with alcoholic iodides and potash. On oxidation with potassium permanganate, the ether is converted into carbonic, oxalic, and acetic acids, and a solid compound which is decomposed by hydrochloric acid at  $190^\circ$  into ethyl chloride and pyrogallol.

From these facts, the author concludes that the tannic acid from oakbark is a condensation-product of an aldehyde,  $C_2H_5.CO.CH_2.CHO$ , with tannin. W. C. W.

**Diphenylparaxylylmethane and its Products of Oxidation.** By W. HEMILIAN (*Ber.*, 16, 2360—2379).—*Diphenylparaxylylmethane*,  $CHPh_2.C_6H_3Me_2$ , is obtained by heating together benzhydrol, paraxylene, and phosphoric anhydride. It is a solid, crystallising from ether in large shining transparent prismatic crystals, which melt at  $92^\circ$ , and are easily soluble in alcohol, ether, benzene, and glacial acetic acid. Like triphenylmethane, it yields colouring matters similar to rosaniline, by successive nitration, oxidation, and reduction. On careful oxidation with chromic mixture, it yields a resinous mass, which is partly soluble in concentrated soda solution; the residue, when extracted with boiling alcohol, yields methyldiphenylphthalide, the first homologue of diphenylphthalide described by Baeyer (*Abstr.*, 1880, 650).

*Methyldiphenylphthalide*,  $Ph_2C<\overset{C_6H_3Me}{\underset{O}{\text{---}}}>CO$ , crystallises from

alcohol in large shining prismatic crystals, is sparingly soluble in cold, more easily in hot alcohol. It melts at  $179^{\circ}$ , and sublimes without decomposition at  $360^{\circ}$ .

*Tolyldiphenylmethanecarboxylic acid*,  $\text{CPh}_2(\text{OH})\cdot\text{C}_6\text{H}_5\text{Me}\cdot\text{COOH}$ , is obtained by first heating methylphenylphthalide with alcoholic soda, and then reducing the resulting sodium tolyldiphenylcarbinolortho-carboxylate,  $\text{CPh}_2(\text{OH})\cdot\text{C}_6\text{H}_5\text{Me}\cdot\text{COONa}$ , with zinc-dust; the solution so obtained is decomposed by an acid, when the tolyldiphenylmethanecarboxylic acid separates out as a white curdy precipitate. It crystallises from a mixture of alcohol and ether in large transparent tables, insoluble in water, but soluble in alcohol, ether, &c.; it melts at  $217^{\circ}$  and distils without decomposition. It is a strong monobasic acid, forming well-defined salts, which are mostly insoluble in water, but soluble in alcohol. By careful oxidation, it is easily reconverted into methylphenylphthalide.

*Methylphenylanthranol*,  $\text{C}_6\text{H}_5\text{Me} \begin{array}{c} \text{CPh} - \\ | \\ \text{C}(\text{OH}) \end{array} \text{C}_6\text{H}_4$ , is obtained by the

action of concentrated sulphuric acid on tolyldiphenylmethanecarboxylic acid, a formation exactly analogous to that of phenylanthranol (Baeyer, *loc. cit.*). It crystallises from alcohol in light yellow shining tables which melt at  $156^{\circ}$ . It is soluble in ether, hot alcohol, and glacial acetic acid, insoluble in solutions of caustic alkalis, and of the carbonates of the alkali metals, but soluble in boiling alkalis.

*Methylphenyloxanthranol*,  $\text{C}_6\text{H}_5\text{Me} \begin{array}{c} \text{CPh}(\text{OH}) \\ \text{CO} \end{array} \text{C}_6\text{H}_4$ , formed by oxidising methylphenylanthranol with chromic acid. By crystallisation first from glacial acetic acid, and then from alcohol, it is obtained in colourless rhombic tables melting at  $195^{\circ}$ , and soluble in alcohol, ether, and glacial acetic acid, but insoluble in caustic alkalis. Like phenyloxanthranol (Baeyer, *loc. cit.*), it dissolves in concentrated sulphuric acid, forming a purple solution, which becomes dark violet on warming. By reducing agents, it is converted into methylphenylanthranol.

*Methylphenylanthracene*,  $\text{C}_6\text{H}_5\text{Me} \begin{array}{c} \text{CPh} \\ \text{CH} \end{array} \text{C}_6\text{H}_4$ , is obtained by heating methylphenylanthranol with zinc-dust. When crystallised from alcohol or glacial acetic acid, it forms tufts of yellow crystals which melt at  $119^{\circ}$ ; its ethereal and alcoholic solutions exhibit distinct greenish-blue fluorescence. It forms a compound with picric acid, and when treated with sulphuric acid, is converted into a soluble sulphonic acid. Chromic acid converts it into the oxanthranol.

*Tolyldiphenylmethane*,  $\text{CHPh}_2\cdot\text{C}_6\text{H}_4\text{Me}$ , is formed by distilling barium tolyldiphenylmethanecarboxylate with baryta. It crystallises in long thin needles, united in globular masses, melting at  $62^{\circ}$ , and volatile without decomposition at temperatures above  $360^{\circ}$ . It is easily soluble in alcohol, ether, benzene, and glacial acetic acid; its solutions exhibit well-defined blue fluorescence, which is observable in the crystals also. The crystals of this hydrocarbon exhibit the remarkable property of giving out an intensely blue light when

rubbed. In its chemical behaviour the hydrocarbon resembles triphenylmethane and diphenylparaxylylmethane. On oxidation with chromic mixture, it yields a *triphenylcarbinolcarboxylic acid*,  $\text{CPh}_2(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ , melting at  $160\text{--}162^\circ$ .

This hydrocarbon is the third known, having the formula



E. and O. Fischer obtained one containing the methyl-group, symmetrically disposed as regards the methane residue, viz., in the position [1:4] (*Annalen*, **194**, 242). A second one has also been obtained by these chemists from leucaniline; it melts at  $59\text{--}59.5^\circ$ , and on oxidation yields a carbinol melting at  $150^\circ$ . In this hydrocarbon the position of the methyl-group to the methane residue is supposed to be the unsymmetrical one, viz., [1:3]. The author contends that this hydrocarbon is an ortho-compound, and that the tolyldiphenylmethane described by him is in reality the meta-compound, inasmuch as the acid from which it is formed can only have the constitution



and consequently the tolyldiphenylmethane formed from it must have the constitutional formula  $[\text{CHPh}_2 : \text{Me} = 1 : 3]$ . The portion of the products of oxidation of methyl-diphenylphthalide, which is soluble in soda, contains the sodium salts of tolyldiphenylcarbinolmetacarboxylic acid and triphenylmethaneanhydrocarboxylic acid.

*Tolyldiphenylcarbinolmetacarboxylic acid*,



crystallises from hot glacial acetic acid in small leaflets; it is sparingly soluble even in hot alcohol and glacial acetic acid, and insoluble in the cold; it melts at  $250\text{--}255^\circ$ , and is at the same time resolved into water and a yellow non-crystalline product. It forms well-defined crystalline salts, most of which are insoluble in water. Heated with acetic anhydride, it is partially converted into an acetic compound,  $\text{C}_{21}\text{H}_{17}(\text{Ac})\text{O}_3$ .

*Triphenylmethane-anhydrocarboxylic acid*,  $\text{CPh}_2\left\langle \frac{\text{C}_6\text{H}_3(\text{COOH})}{\text{O}} \right\rangle \text{CO}$ ,

is obtained from the mother-liquors obtained in the purification of the tolyldiphenylcarbinolmetacarboxylic acid, from which it differs by being much more easily soluble in alcohol and glacial acetic acid: it crystallises in two distinct forms from its solutions in the latter solvent; by quickly cooling the hot saturated solution, it is obtained in silky needles, and by slow evaporation in transparent tablets; both forms melt at  $244\text{--}246^\circ$ , and distil at higher temperatures without decomposition. It is a monobasic acid, forming salts which as a rule are easily soluble in water. When distilled with excess of caustic alkalis, it yields benzophenone and benzene, the latter being a secondary product of the decomposition of terephthalic acid and benzoic acid. This decomposition is exactly analogous to that which phenolphthalein undergoes under similar conditions.

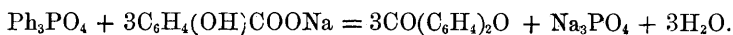
*Triphenylmethanedicarboxylic acid*,  $\text{CHPh}_2\cdot\text{C}_6\text{H}_3(\text{COOH})_2$ . — This acid is obtained by treating the solution of triphenylmethaneanhy-

drocarboxylic acid in caustic soda with zinc-dust, and filtering from excess of zinc, then decomposing the solution with hydrochloric acid. The white curdy precipitate so obtained is next crystallised from glacial acetic acid, when it forms slender needle-shaped crystals melting at 278—280°, and easily soluble in alcohol, ether, and glacial acetic acid. It is a dibasic acid, forming salts which are generally soluble in water; the silver salt is insoluble in water and alcohol. When distilled with an excess of an alkali, it yields triphenylmethane. On oxidation, it is converted into triphenylmethane-anhydrocarboxylic acid. It dissolves in cold concentrated sulphuric acid, forming a greenish-yellow solution, which on warming changes first to green, then indigo-blue, violet, and finally assumes an intense purple.

P. P. B.

**Carbonyldiphenyl Oxide and Hydroxyphenylene Ketone.** By R. RICHTER (*J. pr. Chem.* [2], **28**, 273—309).—In this paper a more detailed account (Abstr., 1882, 618) is given of the ketones obtained originally by Kolbe and Lautemann (*Annalen*, **115**, 197) by the action of phosphorus oxychloride on the basic and neutral sodium salts of salicylic acid.

*Carbonyldiphenyl oxide*,  $\text{CO}(\text{C}_6\text{H}_5)_2\text{O}$ , is best prepared by the action of phenyl phosphate on sodium salicylate:



It is obtained from alcoholic solution in white crystals, which melt at 173—174°, and sublime readily. It is soluble in hot alcohol, benzene, and chloroform, less soluble in cold alcohol and ether, and quite insoluble in water. This ketone is also formed by distilling phenyl phosphate with sodium meta- or para-hydroxybenzoate (with phosphorus oxychloride the reaction is quite different); by acting on potassium methyl salicylate with phenyl phosphate; by distillation of neutral or basic sodium salicylate with phosphorus pentoxide; by dry distillation of sodium chloro-salicylate; by the action of chlorosalicylic chloride on basic sodium salicylate,  $\text{C}_6\text{H}_4\text{Cl}.\text{COCl} + \text{C}_6\text{H}_4(\text{ONa}).\text{COONa} = \text{NaCl} + \text{CO}_2 + \text{CO}(\text{C}_6\text{H}_5)_2\text{O}$ ; and lastly by the action of phosphorus oxychloride on sodium ortho-phenylbenzoate. The ketone character of the compound was demonstrated by the action of hydriodic acid and of zinc-dust; and also by fusion with potash, when it is decomposed into salicylic acid and phenol.

*Methylenediphenyl oxide*,  $\text{CH}_2(\text{C}_6\text{H}_5)_2\text{O}$ , is prepared by the action of hydriodic acid on the ketone, and forms white crystals, soluble in alcohol and ether, sublimable, and melting at 98.5°. It is easily oxidised again to the ketone by dilute nitric acid. By the action of phosphorus pentachloride, a bibasic acid of the formula  $(\text{C}_6\text{H}_5\text{O})_2\text{PO}_3$  is formed, crystallising in needles, and melting at 255—260°. The ammonium and silver salts were prepared; the latter is insoluble in water. Dilute nitric acid decomposes it into phosphoric acid and the original ketone. Bromine gives a substitution-product with methylenediphenyl oxide, and fuming nitric acid a dinitro-derivative of the ketone.

*Carbonyldihydroxydiphenyl*,  $\text{CO}(\text{C}_6\text{H}_4.\text{OH})_2$ , is formed as an inter-

mediate compound on fusing carbonyldiphenyl oxide with potash. With strong bases, it forms salts in which one atom of hydrogen is replaced by the metal, but with alcohol and acid radicals, at high temperatures, it forms compounds in which two hydrogen atoms are replaced. The author has prepared the barium and ammonium salts, and also a mono- and a di-methyl ether, an acetyl-compound,  $C_{13}H_3O_3\bar{A}c$ , and a benzoyl compound. In his opinion this substance is not an acid containing the group  $COOH$ , as Merz and Werth have supposed (*Ber.*, **14**, 192), since no ether could be obtained by long action of hydrochloric acid on the substance dissolved in absolute alcohol, and from the nature of the above-mentioned salts and ether, the two hydroxyls are not of the same kind, but are similar in character to those in the glycols. Dilute nitric acid converts this substance into the original ketone. On heating it with fuming hydriodic acid and amorphous phosphorus, methylenediphenyl oxide is first formed by reduction, and finally the phosphoric acid compound,  $C_{13}H_9O.PC(OH)_2$ . It differs from the ketone in being completely decomposed by fuming hydrochloric acid at  $200^\circ$  into phenol and carbonic anhydride. By reduction with sodium-amalgam, a crystalline substance,  $C_{26}H_{18}O_3$ , is formed. Since acetic anhydride decomposes it into the ketone and methylenediphenyl oxide; its formula may be represented as  $\left\{ \begin{array}{l} (C_{12}H_8O)''CO \\ (C_{12}H_8O)''CH_2 \end{array} \right\}$ .

By oxidation with chromic acid in glacial acetic acid or by permanganate of potash, the ketone is slowly but completely decomposed. It forms a dibromo-substitution product with bromine, and with nitric acid,  $\alpha$ -carbonyldinitrodiphenyl oxide, melting at  $145$ – $150^\circ$ , and  $\beta$ -carbonyldinitrodiphenyl oxide, melting at  $260^\circ$ .

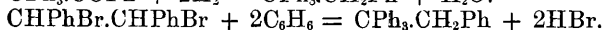
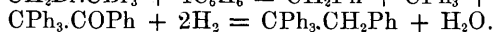
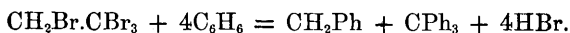
*Hydroxydiphenylene ketone*,  $CO \left\langle \begin{array}{c} C_6H_3(OH) \\ -C_6H_4- \end{array} \right\rangle$ .—This ketone is formed by the action of phosphorus oxychloride on neutral sodium salicylate, and differs in being easily soluble in alcohol, ether, and alkaline carbonates. It forms colourless needles melting at  $91^\circ$ . It can also be obtained by the action of phosphorus oxychloride on methyl or ethyl salicylate. By treating a mixture of basic sodium salicylate and ethyl salicylate with phosphorus oxychloride, a mixture of the two ketones is obtained. Distilled over red-hot calcium oxide, it is decomposed into diphenylene oxide and diphenyl ketone. Over red-hot zinc-dust, it yields a substance smelling of diphenyl, soluble in caustic soda and reprecipitated by acids, and crystallising in beautiful colourless plates. The melting point of this substance is  $51^\circ$ ; diphenyl, melting at  $71^\circ$ , was also obtained. This ketone is not reduced by zinc or sulphuric acid, or by fuming hydriodic acid and phosphorus. Chromic acid completely oxidises it. The author has prepared a mono- and a di-nitro-derivative, also a disulpho- and a monobromo-substitution compound.

*Action of Phosphorus Oxychloride on Neutral Potassium Salicylate and Sodium Meta- and Para-hydroxybenzoates*.—The action on potassium salicylate is the same as on the sodium salt. Sodium meta-hydroxybenzoate gives a yellow crystalline acid, melting and decomposing at  $285^\circ$ . The para-salt gives a chlorinated sublimable or

crystalline compound, melting and distilling at 105°. These reactions will form the subject of future research.

Amongst the products of the action of phenyl phosphate on sodium salicylate were found phenylbenzoic acid melting at 110—111°, diphenyloxide melting at 27—28°, and a substance, which the author supposes may be phenylene oxide ( $C_6H_4O$ ). A. B.

**Unsymmetrical Tetraphenylethane.** By R. ANSCHÜTZ (*Ber.*, **16**, 2377—2379).—By the action of aluminium chloride on a solution of stilbene bromide in benzene, a tetraphenylethane is formed, which is found to be identical with that obtained from unsymmetrical tetrabromethane, benzene, and aluminium chloride (*Ber.*, **16**, 1435), and also with that obtained by the reduction of  $\beta$ -benzopinacolone. The formation of this compound by these three reactions is represented by the following equations:—



The formation of an unsymmetrical tetraphenylethane from symmetrical stilbene bromide is apparently due to an intermolecular change taking place in the stilbene bromide, and brought about by the action of the aluminium chloride on this substance.

P. P. B.

**Bromine-derivatives of  $\beta$ -Naphtholazobenzene.** By L. MARGARY (*Gazzetta*, **13**, 438—440).—The author prepared  $\beta$ -naphtholazobenzene by the action of diazobenzene chloride on an alkaline solution of  $\beta$ -naphthol, whereby a brown crystalline mass was formed, having a green metallic reflex, and after a few hours the whole of the colouring matter separated at the surface of the liquid.  $\beta$ -Naphtholazobenzene forms red-brown needle-shaped crystals, soluble in acetic acid, light petroleum, alcohol, and benzene, and melting at 125—126°, differing thereby from Typke's  $\alpha$ -naphtholazobenzene (*Ber.*, 1877, p. 1550), one modification of which melts at 166°, and the other at 175°.

With the view of determining whether the action of bromine on  $\beta$ -naphtholazobenzene gives rise to a monobrominated derivative, and whether the substitution takes place in the benzene- or in the naphthol-group, the author treated that compound dissolved in acetic acid with bromine in the proportion required to form a monobromo-derivative, whereupon a brown crystalline mass separated, which after two crystallisations from alcohol yielded orange-red silky needles melting at 160—161°, and having the composition  $C_6H_4BrN : NC_{10}H_6.OH$  or  $C_6H_5N : NC_{10}H_6Br.OH$ . In this respect  $\beta$ -naphtholazobenzene differs from the  $\alpha$ -compound, which, according to Typke, does not yield a monobromo-derivative when similarly treated.

This being established, the position of the bromine in the molecule may be determined by subjecting the monobromo-compound to Nietzki's reaction for the preparation of the amidonaphthols: for if the bromine replaces an atom of hydrogen in the naphthol-group, the product

will be a bromamidonaphthol, whereas if the substitution takes place in the benzene-group, the result will be the formation of bromanilines. Experiment showed that the reaction took place in the manner last mentioned, the products being parabromaniline and amidonaphthol, the presence of which latter was demonstrated by converting it, according to Liebermann and Jacobsen's method, into naphthaquinone. As a confirmation of this result, the author diazotised parabromaniline, and treated  $\beta$ -naphthol with the product, obtaining thereby a body agreeing in crystalline form and melting point with the above-described product formed by direct bromination.

H. W

**Products of the Decomposition of Santonous Acid.** By S. CANNIZZARO (*Gazzetta*, 13, 385—395).—This acid heated in a stream of carbonic anhydride at  $330$ — $320^\circ$ , gives off a few gas-bubbles, and yields a liquid distillate together with a crystalline substance saturated with oil, which condenses in the neck of the retort. At  $360^\circ$  a fresh portion of liquid acid is obtained, together with a crystalline matter and a considerable quantity of viscid yellowish oil; and on continuing the heating at a temperature above  $360^\circ$  till nothing is left but a small carbonaceous residue, an oil distils over similar to that above mentioned, and bubbles of combustible gas are given off.

The portion which distils up to  $360^\circ$  contains water, santonous acid, propionic acid, dimethylnaphthol dihydride,  $C_{12}H_{14}O$ , dimethylnaphthol,  $C_{12}H_{12}O$ , and an oil resolvable by potash into propionic acid and dimethylnaphthol dihydride, consisting therefore of the propionic ether of the latter. The portions which distil above  $360^\circ$  consist chiefly of this ether, together with a small quantity of dimethylnaphthalene,  $C_{12}H_{12}$ . The residue left in the retort when the heat has not been raised above  $300^\circ$ , and has been discontinued after water, santonous acid, and traces of other products have passed over, is an anhydride of santonous acid, which solidifies to a transparent brittle resin not perceptibly soluble in alcohol or ether: it dissolves, however, when heated for some time with alcoholic potash, and on evaporating the alcohol and replacing it by water, an alkaline solution is obtained, from which carbonic acid does not separate any phenol, and hydrochloric acid throws down santonous acid. This acid is also found in the residue left after heating to  $360^\circ$ . If the temperature has been raised from that point to  $400^\circ$ , the residue consists of a mixture of  $C_{12}H_{12}O$  and  $C_{12}H_{14}O$ ; but if it has been raised above  $400^\circ$ , the residue is small in quantity, and does not contain any determinable product.

The formation of these products appears to take place as follows: 1. Part of the santonous acid  $C_{15}H_{20}O_3$ , is resolved into water and the anhydride  $C_{15}H_{18}O_2$ . 2. A small portion of the santonous acid is carried over unaltered by the aqueous vapour, and another portion is split up into propionic acid and dimethylnaphthol dihydride,  $C_{15}H_{20}O_3 = C_3H_6O_2 + C_{12}H_{14}O$ . 3. When all the water that can form has been given off, the anhydride,  $C_{15}H_{18}O_2$ , is transformed by the action of heat into the propionic ether of dimethylnaphthol dihydride,

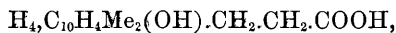




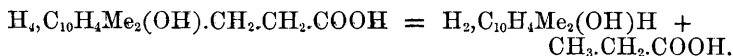
4. The dimethylnaphthol which is formed in variable quantity, and the small quantity of dimethylnaphthalene obtained towards the end of the process, are secondary products of the decomposition of the methylnaphthol dihydride.

Dimethylnaphthol dihydride,  $C_{12}H_{14}O = H_2.C_{10}H_5Me_2.OH$ , is prepared by decomposing its propionic ether with alcoholic potash, evaporating the alcohol, saturating with carbonic anhydride, and distilling in a current of steam. When purified by solution in alcohol and precipitation with water, it crystallises on cooling in very slender silky needles, which after two or three recrystallisations melt constantly at  $113^\circ$ . It is very soluble in ether, alcohol, benzene, and petroleum, especially when hot, nearly insoluble in cold water. It is volatile, and distils unaltered with vapour of water. When treated with phosphorus pentasulphide, it gives up 1 mol.  $H_2O$ , and is converted into dimethylnaphthalene,  $C_{12}H_{12}$ , identical with that which is obtained from dimethylnaphthol, and therefore analogous in constitution to Glaser's dibromonaphthalene melting at  $81^\circ$ . When heated with sulphur in a test-tube, it is partly decomposed, with evolution of hydrogen sulphide and formation of dimethylnaphthol,  $C_{10}H_5Me_2.OH$ , melting at  $134^\circ$ .

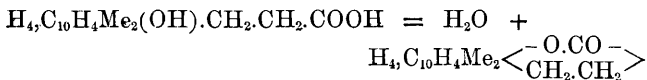
The results above described, and those previously observed by Cannizzaro and Carnelutti (Abstr., 1883, 77), may be explained by regarding santonous acid as a tetra-substituted derivative of naphthalene tetrahydride,  $H_4C_{10}H_8$ , represented by the formula



which is that of a tetrahydride of dimethylhydroxynaphthylpropionic acid. On heating it, two out of the four additive hydrogen-atoms are detached, and employed in separating the propionic acid residue, the products thereby formed being dimethylnaphthol dihydride and propionic acid, thus—



The resinous substance formed by elimination of a molecule of water from santonous acid may be regarded as an inner anhydride, in which the propionic residue, having lost its acid hydroxyl, has attached itself to the phenolic oxygen, as in the phenolic ethers, a change which may be represented by the following equation:—

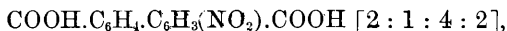


When this anhydride is heated, two out of the four additive hydrogen-atoms may be supposed to separate the propionic residue from the naphtholic nucleus, leaving it attached by the oxygen as an acid radicle, and thereby forming the propionic ether of dimethylnaphthol dihydride,  $CH_3.CH_2.COO.C_{10}H_4Me_2.H_2$ . H. W.

**Derivatives of Phenanthraquinone.** By J. STRASBURGER (*Ber.*, 16, 2346—2348).—Mononitrophenanthraquinone, obtained by nitra-

ting phenanthraquinone (Anschütz and Schultz, *Ber.*, **9**, 1404), yields on nitration a dinitrophenanthraquinone, which is converted by oxidising agents into the  $\alpha$ -dinitrophenic acid melting at  $253^\circ$ , and in which Schultz has shown that both nitro-groups occupy the para-position (*Annalen*, **196**, 29). Hence mononitrophenanthraquinone must have the constitutional formula  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{C}_6\text{H}_3.\text{NO}_2$  [4].

*Paramononitrodiphenic acid*,



is obtained by oxidising the above mononitrophenanthraquinone. It forms yellow prismatic needles melting at  $217^\circ$ . On reduction with tin and hydrochloric acid, it yields an amido-derivative; the hydrochloride of this, when distilled with lime, yields *para-amidofluorene*,

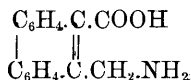
$\text{NH}_2.\text{C}_6\text{H}_3 < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH}_2 \end{smallmatrix} >$ , which crystallises from alcohol in pale-brown needles melting at  $123^\circ$ .

P. P. B.

### Hydrocyanides of the Diketones, and their Saponification.

(Preliminary Notice.) By F. R. JAPP and N. H. J. MILLER (*Ber.*, **16**, 2416—2418).—When *benzil hydrocyanide*, prepared according to Zinin's method, is treated with hydrochloric acid gas, it yields a substance crystallising from benzene in pale yellow needles melting at  $196^\circ$ , and having the formula  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}$ , also an acid containing nitrogen, which crystallises from water in prisms melting at  $185^\circ$ .

*Phenanthraquinone Hydrocyanide*,  $\text{C}_{14}\text{H}_8\text{O}_2(\text{HCN})_2$ .—Phenanthraquinone is treated with aqueous hydrocyanic acid (30 per cent. HCN), and the solution filtered from unaltered phenanthraquinone. The new compound separates in slender needles which easily decompose when moist. It is freed from phenanthraquinone by washing with chloroform, and then dried over concentrated sulphuric acid. When saponified with hydrochloric acid, it yields a compound crystallising from benzene in colourless silky needles, which melt at  $241^\circ$ , and have the composition  $\text{C}_{16}\text{H}_{11}\text{NO}$ . At the same time an acid of the formula  $\text{C}_{16}\text{H}_{13}\text{NO}_2$  is formed; this melts at  $183^\circ$ , and its constitution is probably—



The compound  $\text{C}_{16}\text{H}_{11}\text{NO}$  is probably the lactame or lactime of this acid.

P. P. B.

### Anthracene-carboxylic Acid from Methylanthraquinone.

By E. BÜRNSTEIN (*Ber.*, **16**, 2609—2613).—One part of the crude methylanthraquinone (*Abstr.*, 1883, 70) crystallised from alcohol is mixed with concentrated sulphuric acid (6 parts), water (1 part) added, and then powdered potassium dichromate ( $2\frac{1}{2}$  parts) in small quantities at a time. The mass must be continually stirred during the reaction, which is very violent, and after all the chromate has been introduced the product is heated for some time at about  $110^\circ$ —

120°, water being added if necessary. When cold, the product is washed, boiled with dilute ammonia until the ammoniacal odour disappears and the filtrate acidulated, when the anthraquinonecarboxylic acid is precipitated. The residue insoluble in ammonia is a mixture of anthraquinone and methylanthraquinone. The anthraquinonecarboxylic acid is warmed with an excess of dilute ammonia and twice its weight of zinc-dust gradually added; the filtrate is dark yellow by transmitted light, and exhibits a strong blue fluorescence. On the addition of a mineral acid, anthracenecarboxylic acid is thrown down as a voluminous yellow precipitate; it is sparingly soluble in cold, more readily in hot alcohol, the solution showing an intense blue fluorescence. It crystallises from alcohol in small yellow scales, soluble in glacial acetic acid, sparingly in chloroform, and almost insoluble in benzene and carbon bisulphide; it melts at about 280°, and sublimes, forming small scales and needles. The alkali salts are readily soluble in water, the barium salt almost insoluble. The ethyl derivative crystallises in white scales melting at 134–135°, showing that the acid is identical with the anthracenecarboxylic acid obtained by Liebermann and Bischof (Abstr., 1880, 399), in which the carboxyl-group has the same position as the hydroxyl-group in hydroxyanthraquinone. The *chloride*,  $C_{15}H_9OCl$ , forms a yellow solution with benzene, showing an intense green fluorescence, and yielding the chloride in nodules on evaporation; it also dissolves readily in chloroform, carbon bisulphide, ether and alcohol, and is readily decomposed by boiling with water. The *amide*,  $C_{15}H_{11}NO$ , crystallises from glacial acetic acid in lustrous pale yellow scales, insoluble in water, benzene, carbon bisulphide, and chloroform; it is sparingly soluble in alcohol, from which it crystallises in slender yellow needles, melting at 293–295°. Its solutions show a blue fluorescence. By the action of sodium-amalgam or of hydriodic acid and amorphous phosphorus on the acid, hydro-derivatives are obtained. When an alcoholic solution of the acid is warmed with sodium-amalgam, and acetic acid added from time to time to diminish the alkalinity, the solution becomes gradually decolorised. The *dihydro-* and *tetrahydroanthracenecarboxylic acids* obtained are separated by crystallisation from alcohol, the former,  $C_{15}H_{12}O_2$ , separating first in star-like groups of colourless scales readily soluble in the ordinary solvents; it shows a faint blue fluorescence both in solution and when dry; its alkali salts are readily soluble, those of the alkaline earths and heavy metals sparingly soluble; it melts at 203°. *Tetrahydroanthracenecarboxylic acid*,  $C_{15}H_{14}O_2$ , is more readily soluble in alcohol than the last-mentioned acid, and crystallises in colourless lustrous rhombic plates melting at 164–165°, and showing no fluorescence. By the action of hydriodic acid (sp. gr. 1.7) and amorphous phosphorus at 220–230°, a mixed product is formed, and on fractionally crystallising it from alcohol, *hexhydroanthracenecarboxylic acid*,  $C_{15}H_{16}O_2$ , is obtained melting at 232°; it crystallises from benzene, chloroform, and carbon bisulphide in slender colourless needles, and from alcohol in nodules; in solution, it shows a faint blue fluorescence. The more soluble fractions melt between 150° and 200°, and appear to contain the tetrahydro-acid.

A. K. M.

**Phellandrium Aquaticum.** By L. PESCI (*Gazzetta*, 13, 496).—This plant yields an essential oil, about 80 per cent. of which consists of a terpene (*Phellanthrene*) boiling at 103–104° under a pressure of 80 mm., and at 171–172° under 766 mm. Sp. gr. 0.8558 at 10°. Refractive index for D = 1.481. Rotatory power  $[\alpha]_D = -16.74$ . The author has not succeeded in obtaining pure hydrochlorides. Phellanthrene heated at 140–150° in sealed tubes is converted into a transparent neutral solid substance, soluble in ether, insoluble in alcohol, melting at 86°, isomeric with the liquid, but differing from it in having a strong dextrorotatory power. H. W.

**Carvol.** By A. BEYER (*Arch. Pharm.* [3], 21, 283–288).—Gladstone has shown that the carvol obtained from dill-oil agrees in its principal physical properties with the carvol from caraway oil. Flückiger found that the carvol obtained from German mint-oil, *Mentha crispa*, differed from the carvol from the other two sources in being strongly lævorotatory. The author has re-examined the carvol obtained from these three oils. To obtain it, the crude oils were distilled, the portion of the caraway oil distilling at 223°, those of the German mint-oil at 215–230°, and 200–215° being employed. The crude dill-oil was used without distillation. The hydrogen sulphide compounds,  $(C_{16}H_{14}O)_2.SH_2$ , were first obtained in the crystalline state and recrystallised from a mixture of three parts of chloroform and one of alcohol. The yield from caraway oil was 8 per cent., that from dill-oil 40 per cent., whilst the first fraction of the mint-oil yielded 50 per cent., the second fraction 30 per cent. All the hydrogen sulphide compounds melted at 187°. The specific rotatory power  $[\alpha]_D$  at 20° of the compound from caraway oil was + 5.53, from dill-oil + 5.44, from mint-oil – 5.55. No crystallographic difference in the compounds could be detected. By the action of hydrogen sulphide on an alcoholic solution, all the three compounds were converted into the amorphous thiocarvol  $(C_{16}H_{14}S)_2.SH_2$ . The carvol obtained from all the hydrogen sulphide compounds agreed in boiling point and density; and the specific rotatory power of carvol from caraway-oil and dill-oil was nearly the same, being dextrorotatory; the carvol from mint-oil, however, was lævorotatory ( $[\alpha]_D = -62.46$  at 2°).

The carvol from mint-oil was distilled from metaphosphoric acid, the resulting *carvacrol* dissolved in potash solution, filtered, decomposed with sulphuric acid, and the *carvacrol*,  $C_{10}H_{14}O$ , was dried over calcium chloride. It solidified at – 20° to a crystalline mass. The boiling point was 230–231°; sp. gr. at 4° 0.975, specific rotatory power 0. The crystalline barium salt of *carvacrolsulphonic* acid was also prepared. It was thus shown that the *carvacrol* from lævorotatory carvol is identical with the *carvacrol* from dextrorotatory carvol. A small quantity of a hydrocarbon boiling at 168–171° was obtained from the mint-oil. It was lævorotatory, and appeared to be a terpene. W. R. D.

**Cinchocerotin.** By A. HELMS (*Arch. Pharm.* [3], 21, 279–283). This substance was exhibited by its producer, Kerner, at the exhibitions at Paris in 1858 and at London in 1862. It had been deposited

in copper tubes through which hot alcohol was passed after having exhausted a mixture of calcium hydroxide and South American calisaya bark. The brown mass yielded two different substances when treated with alcohol, the first and larger constituent was a white crystalline body, for which the author proposes to retain the name *cinchocerotin*, the second a light yellow substance of which only a small quantity was obtained. The first constituent is represented by the formula  $C_{27}H_{48}O_2$ , and melts at  $130^\circ$ . It is dissolved by the ordinary solvents, and when oxidised with chromic mixture, yields butyric and acetic acids, together with an acid which was obtained in crystals melting at  $72^\circ$ . This the author proposes to call *cinchocero-tic acid*,  $C_{10}H_{22}O_2$ . Cinchocerotin is not attacked by alkalis, and is probably allied to betulin and cerin in constitution. The second constituent of the crude mass is decomposed at  $230^\circ$  without melting, and when heated with glacial acetic acid forms a crystalline acid melting at  $54^\circ$ , which is easily soluble in alcohol, ether, and light petroleum. It forms sparingly soluble metallic salts. A further examination of this constituent was not possible owing to the small yield.

W. R. D.

**Piscidin, the Active Principle of Jamaica Dogwood.** By E. HART (*Amer. Chem. J.*, 5, 39—40).—Fluid extract of Jamaica dogwood was mixed with lime, left at rest for half an hour in a warm place, filtered, and water added to the filtrate from which, after 2—3 days, crystals of piscidin separate. After purification, it is obtained in nearly colourless microscopic crystals of the formula  $C_{23}H_{24}O_8$ , and melting at  $192^\circ$  (uncorr.). It is insoluble in water, slightly soluble in ether or cold alcohol, much more soluble in boiling alcohol, readily in benzene and chloroform. It dissolves in strong hydrochloric acid, and is reprecipitated by water apparently unchanged. It does not seem to be a glucoside, and gives no precipitate with lead acetate. The alcoholic solution is neutral in reaction.

A. J. G.

**Action of Nitric Acid on Teucrin.** By A. OGLIALORO (*Gazzetta*, 13, 498).—In his memoir on *Teucrium fruticans* (Abstr, 1879, 728), the author showed that teucrin, the glucoside of this plant, when treated with dilute nitric acid, is converted into a monobasic acid,  $C_8H_8O_2$ , melting at  $180^\circ$ . Further experiments on this acid and its derivatives have shown that it is identical with anisic acid.

H. W.

**Saponin from "Saponaria officinalis."** By C. SCHIAPARELLI (*Gazzetta*, 13, 422—430).—The analyses hitherto made of saponin obtained from different plants are not very concordant, the results varying indeed from 47.52 per cent. C and 7.16 H (Overbeck) to 52.63 C and 7.48 H (Rochleder and Schwarz). Moreover the experiments of the last-named chemist lead to the conclusion that the carbohydrate obtained in the first instance from saponin by decomposition with acids, is not grape-sugar, but a body convertible into that sugar by the further action of acids,—and consequently that saponin is not a glucoside but an amyloid. To throw further light on this matter, the author has endeavoured to determine whether the

products extracted from different plants and included under the name of saponin, are really identical, and in the present paper he describes the results obtained with saponin from *Saponaria officinalis*.

The root of this plant, dried and coarsely pounded, was boiled for three days in a reflux apparatus with alcohol of 90°; after which the boiling alcoholic decoction was separated and left for some days in a cool place, whereupon the sides of the vessel became coated with a copious yellow flocculent deposit which, when freed from colouring matter by treatment with a warm mixture of alcohol and ether, consisted of saponin, still however very impure. Treatment with alcohol and animal charcoal still left it contaminated with about 3 per cent. of mineral matter. It was therefore dissolved in the smallest possible quantity of water; the cold solution was precipitated with saturated baryta-water; the resulting barium saponate, after washing with baryta-water, was suspended in water and decomposed by a current of carbonic anhydride, then heated to the boiling point, and filtered; the filtrate evaporated to a syrup at a gentle heat was precipitated with alcohol; and the still yellowish saponin was further purified with alcohol of 90 per cent. The substance thus obtained still contained barium salts, to remove which it was dissolved in water and treated with dilute sulphuric acid, added drop by drop; and the filtered liquid, after concentration at a gentle heat, was precipitated with alcohol and ether, these operations being repeated a second and a third time, and the product finally purified with boiling alcohol of 90 per cent. in quantity not sufficient to dissolve it completely. The alcoholic solution evaporated in a vacuum left perfectly white flocks of pure saponin, which were washed with ether and dried over sulphuric acid.

Saponin thus prepared gave, as the mean result of five analyses, 52.65 per cent. carbon and 7.36 hydrogen, agreeing nearly with the formula  $C_{32}H_{54}O_{18}$ , which requires 52.86 C and 7.44 H. Saponin from *Gypsophila* was found by Rochleder to contain 52.65 carbon and 7.34 hydrogen.

Pure saponin is a very white amorphous inodorous powder, which excites sneezing when inhaled by the nostrils; it has a pungent disagreeable taste, and is poisonous; dissolves very freely in water, but is insoluble in ether, benzene, and chloroform, and only slightly soluble in alcohol. Heated on platinum-foil, it decomposes, emitting an odour of burnt sugar, and leaving a porous residue difficult to burn. Saponin is lævogyrate, like most glucosides; specific rotatory power  $[\alpha]_D = -7.30$ : it is the least optically active of all known glucosides.

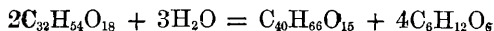
Saponin, as already observed, is remarkable for the power of its aqueous solution to dissolve salts which are insoluble in water. When its aqueous solution, mixed with lead acetate, is precipitated by hydrogen sulphide and filtered, the liquid which passes through is black from dissolved lead sulphide, which may be precipitated from it by adding a small quantity of alcohol. A boiling aqueous solution of saponin dissolves barium carbonate (up to 10 per cent.), which may be precipitated by sulphuric acid; nevertheless barium sulphate is slightly soluble in aqueous saponin. This property of dissolving salts throws great difficulty, as already observed, in the way of purifying saponin.

This substance likewise dissolves gases, and incloses them mechanically. A dilute aqueous solution of saponin forms on agitation a very persistent froth.

An aqueous solution of saponin mixed with hydroxide of potassium, barium, or strontium, yields precipitates of the corresponding compounds. The barium compound has the composition—



*Products of Decomposition of Saponin.*—An aqueous solution of saponin was heated on a water-bath with dilute sulphuric or hydrochloric acid, the liquid being filtered after two hours, in order to remove the flocculent substance which separated, and thereby prevent its further decomposition by the acid; the filtered solution was then again boiled, the new precipitate separated, and these operations were repeated a third time. The three precipitates thus obtained agreed very closely in composition, giving as the mean result of their analysis, 60·65 per cent. carbon and 8·22 hydrogen, numbers agreeing nearly with the formula  $\text{C}_{40}\text{H}_{66}\text{O}_{18}$ , which requires 61·06 carbon, 8·38 hydrogen, and 3·56 oxygen. The decomposition of saponin by dilute acids may therefore be represented by the equation—

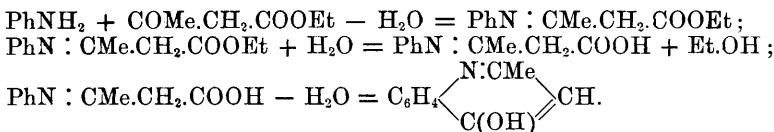


The compound  $\text{C}_{40}\text{H}_{66}\text{O}_{15}$  is called by the author saponetin, to distinguish it from the *sapogenin* of Rochleder and others, which was not of constant composition. Saponetin is a whitish microcrystalline substance, insoluble in water, alcohol, and ether.

The glucose formed by the action of dilute acids on saponin is dextrogyrate, its specific rotatory power being  $[\alpha]_D = +52\cdot48$ . It is fermentable, has a saccharine taste, and has not yet been crystallised, its solution, after concentration to a syrup, having remained for six months without giving any sign of crystallisation. Further experiments are however required to determine whether it is a peculiar sugar distinct from dextrose, or whether the difference between its optical rotatory power and that of the latter is due to some other cause.

H. W.

**New Synthesis of Quinoline-derivatives. I.** By L. KNORR (*Ber.*, **16**, 2593—2596).—By the action of ethyl acetoacetate on aniline, Oppenheim (*Ber.*, **9**, 1098) obtained diphenylcarbamide, alcohol, and acetone. Different results are obtained on modifying the conditions of the experiment. At the ordinary temperature a layer of water separates after some days, whilst a heavy oil is formed which appears to be the condensation-product  $\text{PhN} : \text{CMe} \cdot \text{CH}_2 \cdot \text{COOEt}$ . Aniline and ethyl acetoacetate react more readily when the mixture is heated nearly to the boiling point. When the mass becomes dark yellow the reaction should be interrupted; the product is then treated with concentrated sulphuric acid, diluted with water, and alkali added, when *hydroxymethylquinoline*,  $\text{C}_{10}\text{H}_9\text{ON}$  (m. p.  $222^\circ$ ), is precipitated. The author explains its formation thus :—



If the reaction be conducted in a sealed tube at  $120^\circ$ , a substance of the formula  $\text{C}_{10}\text{H}_{11}\text{NO}_2$  (m. p.  $81^\circ$ ) can be isolated, and is probably anilacetoacetic acid,  $\text{PhN} : \text{CMe.CH}_2.\text{COOH}$ ; it yields hydroxymethylquinoline when treated with sulphuric acid. Hydroxymethylquinoline is sparingly soluble in water, more readily in hot alcohol, insoluble in ether; it has both basic and acid properties, but is precipitated by carbonic anhydride from alkaline solutions; it forms a crystalline sodium salt, hydrochloride, sulphate, and platinochloride. When distilled with zinc-dust, it yields  $\alpha$ -methylquinoline, and may therefore be designated  $\gamma$ -hydroxy- $\alpha$ -methylquinoline.

A. K. M.

**Condensation-products of Methylated Quinolines and Pyridines.** By E. JACOBSEN and C. L. REIMER (*Ber.*, **16**, 2602—2608).—It has been shown by the authors (*Abstr.*, 1883, 922) that a yellow dye,  $\text{C}_{18}\text{H}_{11}\text{NO}_2$ , is formed by the action of phthalic anhydride on quinaldine, or on crude coal-tar quinoline, and that similar dyes are also yielded by the homologues of quinaldine and by pyridine. Further investigation shows that the substance obtained from pyridine is due to the presence of picoline, and that pure pyridine, like pure quinoline, is not acted on by phthalic anhydride. They conclude that Traub's quinophthalone (*Ber.*, **16**, 297) is also most probably derived from a methylquinoline, and that it is either identical or isomeric with quinoline-yellow,  $\text{C}_{18}\text{H}_{11}\text{NO}_2$ . *Paramethylquinophthalone*,  $\text{C}_{19}\text{H}_{13}\text{NO}_2$ , is obtained by heating paramethylquinaldine with phthalic anhydride and zinc chloride at  $200^\circ$ , boiling the melt with hydrochloric acid and crystallising from alcohol; it forms long gold-coloured needles melting at  $203^\circ$ , and resembling quinoline-yellow. It is insoluble in water, sparingly soluble in alcohol, readily in glacial acetic and concentrated sulphuric acids; it dyes silk and wool almost exactly like quinoline-yellow. The paramethylquinaldine can be obtained from paratoluidine and aldehyde by Doebner and Miller's method, and purified by fractional distillation and by means of the sparingly soluble chromate  $(\text{C}_{11}\text{H}_{11}\text{N})_2\text{H}_2\text{Cr}_2\text{O}_7$ . It melts at  $55^\circ$  and boils at  $259$ — $261^\circ$ . When coal-tar pyridine is heated with phthalic anhydride and zinc chloride at  $200^\circ$ , and the product treated with hot dilute hydrochloric acid, the greater portion (containing unaltered pyridine) dissolves, whilst the residue, after crystallisation from glacial acetic acid and from alcohol, yields bright yellow silky scales of *pyrophthalone* melting above  $260^\circ$  with partial decomposition. It is almost insoluble in water, sparingly soluble in alcohol, readily in glacial acetic acid. Its formula,  $\text{C}_{14}\text{H}_9\text{NO}_2$ , indicates its derivation from picoline present in the pyridine, thus:  $\text{C}_6\text{H}_7\text{N} + \text{C}_8\text{H}_4\text{O}_3 = \text{C}_{14}\text{H}_9\text{NO}_2 + \text{H}_2\text{O}$ , and experiment proves that it cannot be obtained from perfectly pure pyridine, whilst coal-tar picoline gives an abundant yield. A second substance, apparently of the same com-



position as pyrophthalone, is also formed; it is, however, more readily soluble in alcohol, and crystallises from glacial acetic acid in slender orange-red needles, melting below  $200^{\circ}$ ; it seems probable therefore that two different picolines exist in coal-tar. Both of these phthalones from picoline dye silk and wool yellow, but much fainter than quinoline-yellow.

The fact that only methylated pyridines and quinolines react with phthalic acid indicates that it is the hydrogen of the methyl-group which becomes substituted, and not that of the pyridine nucleus as was previously assumed. In this case quinoline-yellow will have the formula  $C_9H_6N.CH : C_2O_2 : C_6H_4$ . This view is supported by the behaviour of the phthalones on oxidation; for if the substitution took place in the pyridine nucleus, pyridinecarboxylic acids (or quinolinecarboxylic acids) would be expected to result from the decomposition of the phthalyl-group. On heating quinoline-yellow with nitric acid (sp. gr. 1.2), phthalic acid is produced, together with resinous substances, and a second acid containing nitrogen; this latter acid is sparingly soluble in water, very readily in mineral acids. A substance of similar properties is obtained when a mixture of chromic and sulphuric acids is employed, the product in this case, however, contains no phthalic acid. On neutralising with barium hydroxide and evaporating the filtrate, a sparingly soluble barium salt is obtained yielding an acid which crystallises in colourless needles melting at  $157^{\circ}$ . It dissolves very readily in hot, less so in cold water, and very readily in mineral acids; it forms a platinochloride, crystallising in yellowish-red prisms, and when heated with lime emits an odour resembling that of quinoline. It is probably a new quinolinemonocarboxylic acid. Pyrophthalone is also very readily oxidised by nitric acid, yielding phthalic acid and an acid containing nitrogen, which however has not yet been examined.

When quinaldine (1 mol.) is heated with benzaldehyde (1 mol.) and zinc chloride at  $160-170^{\circ}$ , the product dissolved in hot concentrated hydrochloric acid, and poured into water, the hydrochloride of a solid base (*benzylidenequinaldine*) is precipitated in yellowish needles. The free base,  $C_{17}H_{13}N$ , is insoluble in water, sparingly soluble in cold, readily in boiling alcohol, from which it crystallises in colourless lustrous needles melting at  $99-100^{\circ}$ . At a higher temperature, it sublimes without decomposition, its vapour having an odour resembling that of quinoline. Its formation takes place thus:— $C_{10}H_9N + C_7H_6O = C_{17}H_{13}N + H_2O$ . Its salts are sparingly soluble in cold water; the acid chromate,  $C_{17}H_{13}N.H_2Cr_2O_7 + 2\frac{1}{2}H_2O$ , forms slender reddish-yellow needles sparingly soluble even in boiling water. The same base is produced by the action of benzal chloride on quinaldine in the presence of zinc chloride. Benzylidenequinaldine can be readily oxidised, nitric acid (sp. gr. 1.4) yielding a mixture of several acids, from which paranitrobenzoic acid could be isolated. When oxidised with chromic and sulphuric acids, benzoic acid is formed. Picoline also yields a condensation-product with benzaldehyde analogous to that obtained from quinaldine, whilst pure pyridine is not attacked. It is probable therefore that in these reactions the substitution also takes place in the methyl-group, and that benzyldene-

quinaldine has the constitution  $C_9H_6N.CH : CHPh$ . Benzylidene-quinaldine is identical with the base obtained by Wallach and Wüsten (Abstr., 1883, 1097). A. K. M.

**Preparation of Quinaldine on the Large Scale.** By G. SCHULTZ (*Ber.*, 16, 2600—2601).—When aldehyde is added to an aqueous solution of aniline hydrochloride, and the two are allowed to react in the cold, the hydrochloride of a solid base is produced, and on melting this, either alone, or better, with zinc chloride, it is converted into quinaldine. When paraldehyde, acetal, aldol, and similar substances are employed in place of the aldehyde, and other primary aromatic bases in the place of aniline, compounds are obtained which yield bases analogous to quinaldine when melted with zinc chloride. From the product of the action of free aniline on aldehyde a solid base has been isolated, apparently identical with the above. By boiling with hydrochloric acid both are decomposed (although not readily) into aniline and aldehyde, and then converted into quinaldine. The composition of these bases appears to be far from constant, and to vary with the relative proportions of the components. From paraldehyde and aniline hydrochloride, a base was obtained which, after solution in benzene and precipitation with alcohol, had the composition  $C_{18}H_{20}N_2$ , whilst a base obtained in another way had the formula  $C_{14}H_{16}N_2$ , agreeing with Schiff's ethylenediphenamine.

A. K. M.

**Sparteine.** (Preliminary Notice.) By O. BERNHEIMER (*Gazzetta*, 13, 451—454).—This base,  $C_{15}H_{26}N_2$ , was first obtained from *Spartium scoparium* by Stenhouse in 1881, who determined its composition, and was afterwards examined by Mills, who showed that it is a tertiary diamine. The sparteine examined by the author was prepared from *Spartium scoparium* by a slight modification of Stenhouse's method; it distilled to the last drop at  $180-181^\circ$  under a pressure of 20 mm. Its solution in alcohol at  $96^\circ$  has a specific rotatory power  $[\alpha]_D = -14.6$  for a concentration of 23.88 at  $26^\circ$ . It bears a heat of  $200^\circ$  without alteration, but becomes partially carbonised at higher temperatures; is not decomposed by heating in sealed tubes with hydrochloric acid. Bromine acts strongly on sparteine at ordinary temperatures, even when it is largely diluted with ether, forming an undefined resinous mass.

On gradually adding 3 parts iodine dissolved in ether to an ethereal solution of 1 part sparteine, the iodine is decolorised, and a black precipitate is formed, which when separated, washed with ether to remove free iodine, and dissolved in boiling alcohol, separates on cooling in beautiful green needles, having the composition  $C_{15}H_{26}N_2I_3$ . This compound is insoluble in cold water and alcohol, but dissolves readily in those liquids when heated; it is insoluble in ether, permanent in the air, and yields free sparteine when heated with potash.

Sparteine (as sulphate) oxidised with potassium permanganate yields a small quantity of a volatile acid, having the odour of the fatty acids, together with a non-volatile acid having the composition of a *pyridinemonocarboxylic acid*,  $C_5H_4N.COOH$ ; and on distilling a salt of this acid with lime, a volatile base is obtained having all the

properties of pyridine. The author intends to continue his experiments as soon as he is in possession of a larger quantity of material.

H. W.

**Hydrocyanides of Organic Bases.** By A. CLAUS and E. A. MERCK (*Ber.*, **16**, 2737—2748).—Aniline, toluidine, quinine, cinchonidine, and strychnine, dissolve in aqueous hydrocyanic acid. An excess of acid renders the solution very unstable. The salts have not been isolated, as they are decomposed by evaporation in a vacuum. Although the bases are completely withdrawn from these liquids by ether, the solutions are not mere mechanical mixtures, since they yield double cyanides with mercuric cyanide; *e.g.*, when mercuric cyanide is added to a solution of aniline hydrocyanide, white tabular crystals,  $\text{NH}_2\text{Ph}.\text{HCN} + \text{Hg}(\text{CN})_2$ , are deposited, which dissolve in water, alcohol, and ether.

When mercuric cyanide is added to tetramethylammonium iodide, two salts are formed, *viz.*, a white salt of the composition



freely soluble in water, and a yellow salt,  $\text{NMe}_4.\text{CN}.\text{HgICN}$ , sparingly soluble in water. The white salt slowly changes into the yellow isomeride at the ordinary temperature, more rapidly at  $200^\circ$ .

*Tetramethylammonium cyanide*,  $\text{NMe}_4.\text{CN}$ , prepared by the action of barium cyanide on tetramethylammonium iodide, has been described by C. Thompson (*this vol.*, p. 286). The clear crystals of the salt become opaque at  $150^\circ$ , decrepitate at  $215^\circ$ , and melt at  $295^\circ$ . The salt can be volatilised at  $225$ — $230^\circ$  without melting. With mercuric cyanide it forms a double salt,  $\text{NMe}_4.\text{CN}.\text{Hg}(\text{CN})_2$ , crystallising in prisms melting at  $275^\circ$ . The corresponding silver salt,



has been described by Thompson. Tetramethylammonium cyanide dissolves cobalt cyanide and ferrous cyanide, forming tetramethylammonium cobaltcyanide and ferrocyanide respectively. The latter compound has been described by Barth (*Ber.*, **8**, 1484). The former crystallises in yellow plates, and resembles the potassium cobaltcyanide in its properties.

*Cinchonidine ethylcyanide*,  $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}.\text{EtCN}$ , prepared by the action of barium cyanide on cinchonidine ethylsulphate, forms white crystalline needles, which are decomposed by carbonic acid, and rapidly absorb moisture from the air. It is soluble in water but insoluble in ether and chloroform. The crystals melt with decomposition at  $140^\circ$ . *Quinine ethylcyanide*,  $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2.\text{EtCN}$ , crystallises in needles soluble in alcohol. The crystals melt at  $90^\circ$  and begin to decompose at  $95^\circ$ . *Strychnine ethylcyanide*,  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2.\text{EtCN}$ , is less hygroscopic and more stable than the quinine and cinchonidine compounds. It dissolves freely in water, but is less soluble in alcohol.

W. C. W.

**Caffeine Methhydroxide.** By E. SCHMIDT (*Ber.*, **16**, 2587—2588).—In the hopes of obtaining an insight into the constitution of caffeine, the author submitted caffeine methhydroxide to the action of hydrochloric acid. He previously showed (*Abstr.*, 1883, 872 and 873)

that caffeine and theobromine yield the same decomposition-products when treated in this way, but the reaction threw no light on the constitution of these substances. Caffeine methhydroxide,



is readily obtained by the action of moist silver oxide on caffeine methiodide (*loc. cit.*). When it is dissolved in fuming hydrochloric acid, and left for 14—20 days to evaporate spontaneously, amalic acid separates, with simultaneous formation of methylamine and formic acid, the production of amalic acid being, however, due to a secondary decomposition of the dimethylalaluric acid first formed. A considerable portion of the caffeine methhydroxide is also converted into caffeine methylchloride,  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2, \text{MeCl}$ , whilst a smaller portion gives rise to secondary reactions.

Caffeine methhydroxide suffers no appreciable change on continued heating above its melting point (137—138°), but is completely decomposed when submitted to dry distillation in a current of hydrogen, caffeine being produced. Water decomposes it at about 200°, with formation of carbonic anhydride and methylamine. With a solution of bromine in chloroform, it yields a readily decomposable addition-compound which is decomposed by water into hydrobromic acid, methylamine, cholestrophane, and allocaffeine. This last substance is probably methylapocaffeine, since it is decomposed into carbonic anhydride and methylcaffuric acid when boiled with water. By the action of hydrochloric acid and potassium chlorate, caffeine methhydroxide yields dimethylalloxan, allocaffeine, amalic acid, cholestrophane, and methylamine; with chromic mixture it yields carbonic anhydride, formic acid, cholestrophane, and methylamine. Nitric acid (sp. gr. 1.4) decomposes it at ordinary temperatures, with violent evolution of carbonic anhydride and formation of methylamine and cholestrophane. Baryta-water also decomposes it in the cold. A. K. M.

**Quinine Phenolsulphonate.** By P. GIURLEO (*Arch. Pharm.* [3], 21, 298).—This salt can be obtained by dissolving quinine in phenolsulphonic acid and by decomposing solutions of lead or barium phenolsulphonates with a solution of quinine sulphate. The salt, which crystallises with difficulty, contains 52 per cent. of quinine, 20 per cent. of phenolsulphonic acid, and 28 per cent. of water.

W. R. D.

**Berberine.** By E. SCHMIDT (*Ber.*, 16, 2589).—The formula of this body, according to Fleitmann, is  $\text{C}_{42}\text{H}_{36}\text{N}_2\text{O}_8$ , according to Kemp,  $\text{C}_{42}\text{H}_{34}\text{N}_2\text{O}_7$ , according to Stas,  $\text{C}_{44}\text{H}_{38}\text{N}_2\text{O}_{10}$ , according to Henry,  $\text{C}_{42}\text{H}_{38}\text{N}_2\text{O}_{10}$ , and according to Serrius and Hlasiwetz,  $\text{C}_{20}\text{H}_{17}\text{NO}_4, 4\frac{1}{2}\text{H}_2\text{O}$ . From numerous analyses of the free base, the hydrochloride, nitrate, and sulphate, the author assigns to it the formula  $\text{C}_{20}\text{H}_{17}\text{NO}_4, 4\text{H}_2\text{O}$ . Analyses of Hlasiwetz and Gilm's hydroberberine (*Annalen*, Suppl., 2, 191), its hydrochloride and nitrate confirm their formula,  $\text{C}_{20}\text{H}_{21}\text{NO}_4$ . From its behaviour with ethyl iodide, hydroberberine must be a tertiary base. Berberine is converted into berberine hydriodide by treatment

with ethyl iodide. The hydroxide obtained from hydroberberine ethiodide forms colourless needles melting at  $165^{\circ}$ ; it yields crystalline salts with hydrochloric, nitric, and sulphuric acids, and with platinic chloride. On oxidising berberine with alkaline permanganate, a bibasic acid,  $C_{10}H_{10}O_6 + 2H_2O$ , melting at  $165^{\circ}$ , is obtained apparently identical with hemipinic acid.

A. K. M.

**Derivatives of Berberine.** By O. BERNHEIMER (*Gazzetta*, 13, 342—347).—When berberine is heated in a retort with five times its weight of potassium hydroxide, it blackens, intumescs, and gives off ammonia, together with a small quantity of an oily liquid which, on examination, was found to be quinoline. From the residue in the retort, two acids were isolated, which were found to have all the properties ascribed to them by Hlasiwetz and Gilm; the author is at present engaged in studying their constitution.

When hydroberberine is heated with methyl iodide at  $100^{\circ}$  in a closed tube, a yellow crystalline mass is obtained, which may be purified by repeated crystallisation from boiling methyl alcohol. It crystallises in the trimetric system:  $a : b : c = 1.10332 : 1 : 1.78880$ . Observed forms, 001, 111, 113; combinations, 001, 111, 113; cleavage perfect, 001. The *hydroberberine methiodide*,  $C_{20}H_{21}NO_4, MeI$ , is sparingly soluble in water or alcohol in the cold, but readily when heated. When the iodide suspended in water is treated with silver oxide, it yields the corresponding hydroxide, which may be obtained in crystalline crusts,  $C_{20}H_{21}NO_4, MeHO + H_2O$ , on evaporating the solution. It is strongly basic, and liberates ammonia from ammonium chloride. It dissolves in cold alcohol, but is insoluble in ether. On adding hydrochloric acid to its aqueous solution, the chloride is precipitated as a crystalline powder. The platinochloride crystallises in beautiful lustrous plates, soluble in boiling alcohol. When heated in a sealed tube at  $150^{\circ}$ , the hydroxide is decomposed, with elimination of methyl alcohol. From these results, the author infers that hydroberberine, like berberine itself, is a tertiary base.

When berberine is heated with methyl iodide and methyl alcohol, it yields a methiodide,  $C_{20}H_{17}NO_4, MeI$ , in stellate groups of slender needles. On treating this with silver oxide, the corresponding hydroxide is obtained, very similar in its properties to the hydroberberine compound. The platinochloride is a yellow powder.

Fleitmann (*Annalen*, 59, 176) in his paper on berberine mentions the formation of the hydrochloride of a base containing sulphur. The author, following Fleitmann's directions, added yellow ammonium sulphide to a solution of berberine hydrochloride, collected the red precipitate, dissolved it in warm water, and added hydrochloric acid; hydrogen sulphide was evolved, and on examining the solution it was found to contain berberine hydrochloride, but no trace of sulphuretted base. The red precipitate mentioned above is probably a persulphide of berberine.

On treating hydroberberine with iodine, both in chloroform solution, a brownish precipitate is obtained consisting of berberine hydriodide,  $C_{20}H_{17}NO_4, HI$ . It is easily purified by crystallisation from dilute alcohol.

C. E. G.

**Alkaloids of Angustura Bark.** By KOERNER and C. BÖHRINGER (*Gazzetta*, 13, 363—367).—In this preliminary notice the authors, after some historical details as to the introduction of the bark, state that it contains aromatic substances and several alkaloids, the amount of the latter varying in different specimens from 0·8 to 1 per cent. The alkaloids are mostly in the free state, and may be extracted directly from the bark by means of ether. After the ethereal extract has been washed with dilute potash solution, the addition of oxalic acid or dilute sulphuric acid gives a yellow crystalline precipitate of the corresponding salt of one of the alkaloids, *cusparine*, whilst other alkaloidal salts remain in solution.

The precipitated cusparine salt is moderately soluble in boiling alcohol, and, on cooling, crystallises out in slender needles of a magnificent greenish-yellow; this colour is not removed by repeated crystallisation, or by treatment with animal charcoal, and other salts of the alkaloid, obtained from the yellow precipitate by decomposition, are also intensely yellow. If, however, the free cusparine,  $C_{19}H_{17}NO_3$ , obtained from these coloured salts, is crystallised several times from light petroleum, and then reconverted into the salt, this is found to be colourless. The author has been unable to ascertain the cause of this yellow coloration. The alkaloid crystallises from light petroleum in tufts of slender needles melting at  $92^\circ$ ; it is moderately soluble in ether, more readily in alcohol. The sulphate, oxalate, and hydrochloride of the base are but sparingly soluble in water; the acetate is much more soluble, but the solution is decomposed if largely diluted; the tartrate dissolves readily. The platinochloride was obtained as an orange-yellow crystalline precipitate.

When treated with potassium hydroxide, cusparine splits up, yielding a new alkaloid and the potassium salt of an acid which seems to be an aromatic derivative; the acid is sparingly soluble and crystallises readily. The alkaloid crystallises from alcohol, in which it is very sparingly soluble, in minute, very brilliant, colourless needles; it decomposes at  $250^\circ$  without melting. An attempt to decompose the cusparine in a similar manner by the action of hydrochloric acid failed, as it began to carbonise even at  $100^\circ$ .

In the mother-liquors from which the cusparine was originally precipitated as sulphate or oxalate, another alkaloid is found, to which the authors have given the name of *galipeïne*,  $C_{20}H_{21}NO_3$ . The free base crystallises from light petroleum in white needles melting at  $115\cdot5^\circ$ . It may be obtained in well-formed transparent prisms from its solution in ether or alcohol. All the salts of this alkaloid are more soluble than those of cusparine; several of them are of a magnificent greenish-yellow like uranium salts. The sulphate crystallises in large prisms with 7 mols.  $H_2O$ , which it loses in part on exposure to the air; it melts at  $15^\circ$ , and at  $100^\circ$  undergoes decomposition, yielding the sulphate of another alkaloid and a crystalline nitrogenous substance which melts at  $196^\circ$ . The platinochloride crystallises in prisms with a triangular base.

Besides cusparine and galipeïne, the authors have found another alkaloid which melts at  $180^\circ$ , and is very sparingly soluble in ether.

It crystallises from alcohol and furnishes salts, the solutions of which have a blue fluorescence.

The property these alkaloids have of being transformed into other alkaloids with simultaneous formation of acids, is interesting, and may throw some light on the constitution of vegetable alkaloids in general.

C. E. G.

**Ptomaines.** By A. SOLDANI (*Gazzetta*, 13, 325).—In order to obviate the difficulties usually met with in the extraction and purification of ptomaines, the author digests the putrid viscera with alcohol acidified with oxalic acid; the solution is distilled down to remove alcohol, taken up with water, and the acid solution agitated with bisulphide of carbon and with ether. It is then rendered alkaline by lime, and the bases are removed by ether, chloroform, &c. The various extracts are purified by fractional distillation in a current of hydrogen. The author describes the ptomaines as colourless liquids, easily alterable in contact with air, and all more or less soluble in water: some are soluble in ether, others in chloroform. They have a pleasant odour, and the higher the boiling point the stronger the basic properties. It is not known as yet whether these compounds are amides, amines, or true alkaloids.

C. E. G.

**The so-called Ptomaines in Relation to Toxicological Researches.** By F. MARINO-ZUCO (*Gazzetta*, 13, 431—433).—The author's experiments were made on a variety of fresh animal substances, viz., white and yolk of egg, brains, lungs, heart, liver, spleen, and blood, several methods being employed, with strict attention to all the conditions indicated by their respective authors. The result of these experiments was the extraction of a base which exhibited all the usual reactions of the alkaloids, but had the constitution of an ammonium hydroxide, and in those cases in which an aurochloride could be prepared and analysed, was found to be identical in composition with neurine. In one instance traces were also found of the so-called "animal quinine."

To determine the origin of this neurine, the author applied the methods above mentioned to the lecithins (prepared by Strecker's method from egg-yolk), and found that these substances behave in the same manner as, for example, a mass of brain, egg, lungs, &c. On applying the same method to the albumin remaining after complete extraction of the lecithins, the result was purely negative. Hence it is clear that the so-called ptomaines obtained in the extraction of fresh animal substances, originate, not as is generally supposed, from sudden alterations of the proteids, but from the splitting up of the lecithins under the influence of acids or alkalis.

As neurine hydrochloride is not decomposed by sodium bicarbonate, the author was able to determine the toxicological question in cases of the extraction of alkaloids from substances in which putrefaction has not yet commenced. The hydrochlorides of the alkaloid and of the so-called ptomaines, simultaneously extracted, are dissolved in water, and the liquid, rendered alkaline with sodium bicarbonate, is

agitated with the solvent. The neurine then remains dissolved in the water as hydrochloride, and the alkaloïd may then be extracted alone. This has been demonstrated by all the experiments made as above described, and by others on yolk of egg mixed with strychnine.

H. W.

**Selmi's Ptomaines.** By F. MARINO-ZUCO (*Gazzetta*, **13**, 441—451).—In this paper, the author describes a number of experiments, chemical and physiological, tending to establish the conclusion indicated in the preceding preliminary notice, as to the identity of these bases with neurine. The most characteristic chemical reactions observed in both cases are :

- With *Phosphoric acid*: slight brown coloration on heating.  
 „ *Platinic chloride*: no precipitate, but deposition of yellowish crystals after a short time.  
 „ *Mercuric chloride*: white precipitate.  
 „ *Auric chloride*: yellowish precipitate, and after a short time, reduction of metallic gold.  
 „ *Iodised potassium iodide*: red-brown precipitate, which, however, soon redissolves.

H. W.

**Compounds of Silver with Albuminoids.** By O. LOEW *Ber.*, **16**, 2707—2709).—On warming silver albuminate with excess of an ammoniacal solution of silver nitrate, a reddish-brown precipitate of variable composition is deposited. It is purified by solution in dilute ammonia and reprecipitation with dilute sulphuric acid. It is insoluble in water and alcohol, but dissolves in alkalis and in dilute sulphuric acid. The ratio of C to N in the compound is the same as it is in peptone. When the compound is digested with baryta-water or hydrochloric acid, metallic silver is deposited, and a substance resembling peptone remains in solution. The silver is not precipitated from an ammoniacal solution of the compound by sulphuretted hydrogen at the ordinary temperature. In many respects this red-brown compound resembles the substance obtained by the action of a dilute ammoniacal solution of silver on the albumin in the living cells of the alga, *Spirogyra*. The latter compound, however, is insoluble in dilute sulphuric acid, and is not even decomposed by sulphuretted hydrogen in warm solutions.

A compound containing as much as 82.4 per cent. of silver was obtained by adding potash to the ammoniacal solution of silver nitrate and albumin. It is a silver-grey powder, insoluble in water and in dilute acids. It dissolves in ammonia, yielding a deep orange-coloured solution.

The author regards these substances as compounds of varying quantities of molecular silver with partially oxidised silver albuminate.

W. C. W.

**Permanence of Carbonic Oxide Hæmaglobin.** By E. SÄLFELD (*Arch. Pharm.* [3], **21**, 289).—The absorption-spectrum of this compound was obtained from venous blood 14 days after death, and again after the lapse of one month. The blood was treated with



ammonium sulphide, to reduce oxy-hæmaglobin, before examination. After two months, the absorption-spectrum of carbonic oxide hæmaglobin was not observed. W. R. D.

**Gelatin Peptone.** By P. TATARINOFF (*Compt. rend.*, **97**, 713—714).—Pure gelatin is digested with artificial gastric juice at 40°, and when solution is complete, the liquid is saturated with calcium carbonate, boiled, filtered, concentrated, and precipitated by alcohol. After 24 hours, the precipitate is dissolved in cold water, filtered and dialysed after addition of a few drops of hydrochloric acid. The purified solution thus obtained is concentrated, and the peptone precipitated by alcohol. It has the composition :—

	C.	H.	N.
I. ....	50·00	7·26	17·57
II. ....	49·53	7·00	17·69

These numbers show that gelatin undergoes no great alteration under the influence of gastric juice, but appears to combine with the elements of water, like the albuminoids. The same body is obtained by the prolonged digestion of gelatin at a somewhat higher temperature with somewhat stronger hydrochloric acid and without any pepsin. C. H. B.

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## Physiological Chemistry.

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### **Influence of Air somewhat deficient in Oxygen on Animals.**

By C. KEMPNER (*Bied. Centr.*, 1883, 565).—The author finds that the amount of oxygen used up by mammals diminishes when breathing such air: in the case of birds, however, there is either no diminution in the amount of oxygen absorbed, or not to the same extent. The latter have the faculty of compensating for the poorer air by increasing the activity of their respiratory organs. J. T.

**Nutrition of the Dog.** By GUIMARAES (*Compt. rend.*, 97, 645—646).—Dogs fed, under ordinary conditions, on fresh lean beef consumed on an average one-tenth to one-sixteenth of their weight per day; others, to which a strong infusion of coffee was given, consumed from one-ninth to one-eighth their weight; whilst others, which were kept at a temperature of 10—12°, consumed from one-twelfth to one-ninth their weight. Dogs fed on fat pork and tapioca ate only about one-sixtieth of their weight, and rapidly fell off in condition. Others were fed on a mixed diet, consisting of a limited amount of lean beef with a large amount of pork fat. They consumed all the lean beef (180—250 grams per diem) but only a part of the fat, and they gradually fell off in condition, the total daily consumption being from one twenty-fourth to one twenty-second part of their weight, about half of this being carbohydrates. The results were but slightly

affected by the size of the animals; the small dogs generally consumed a slightly higher proportion of food than the large dogs. The faeces amounted to 5—6 grams per diem per kilogram of body-weight for dogs under normal conditions, and 6—7 grams per kilogram for dogs to which coffee had been given, or which had been kept at a low temperature. This is less than 8 per cent. of the weight of food consumed. The total of weight of the animals did not sensibly vary from day to day.

C. H. B.

**Physiological Functions of Maltose.** By E. BOURQUELOT (*Compt. rend.*, **97**, 1000—1003).—A 2 per cent. solution of maltose is not affected, even after 24 hours at 15° or 38°, by saliva or diastase which has been previously filtered through Klebs and Tiegel's apparatus. The same result is obtained in an atmosphere of carbonic anhydride. Maltose is also unaffected by a mixture of saliva or diastase with the invertin of the intestinal juice, and by artificial gastric juice, or natural pancreatic juice. In the latter case, small quantities of glucose are formed after about 10 hours, but this is due to the action of bacteria, which cannot be entirely excluded, since the pancreatic juice cannot be filtered.

Maltose and saccharose, mixed with an unfiltered solution of intestinal juice and kept at 38° for several hours, are partially or completely split up, but if the intestinal juice has been filtered through Kleb's apparatus, no change takes place in either case.

A 1 per cent. solution of maltose is not affected by a 0.2 per cent. solution of hydrochloric acid at 38°, nor by a solution of lactic acid of equivalent strength. A solution of saccharose of the same strength is rapidly inverted by hydrochloric acid, and 33 per cent. is inverted in 36 hours by lactic acid. A similar solution of maltose is not affected by carbonic anhydride at the ordinary pressure and at the temperature of the body, but 3.2 per cent. of the saccharose is inverted in five days under the same conditions.

In all probability, if saccharose is inverted in the small intestine, the active agents are hydrochloric and lactic acids, and if small quantities of saccharose find their way unaltered into the blood, the carbonic anhydride with which the latter is always charged is probably sufficient to cause inversion. Maltose, on the other hand, is not inverted except in the intestine, and the inversion is due either to a zymase, which differs from the invertin of yeast and will not pass through porous earthenware, or to bacteria.

These results do not decide whether maltose is or is not directly assimilated.

C. H. B.

**Formation of Fat in the Animal Organism.** By N. TSCHIRWINSKY (*Landw. Versuchs.-Stat.*, **29**, 317—352).—This investigation was begun when the function of carbohydrates in the system was still an open question, and with the object of determining their influence on the formation of fat in the organism. The experiments were made with two pairs of young pigs, each pair coming from one litter, and carefully selected, after undergoing the same treatment, so as to be as near as possible of the same condition. At the beginning of the series

of experiments one of each pair was killed, and the quantity of fat and albumin present determined. Of the remaining two, one was fed with barley alone, and the other with barley and varying proportions of starch and sugar. The greatest care was taken in the daily analyses and weighing of the food, and the troughs were so made and fitted as to prevent waste. Three times during each series of experiments the digestive coefficient was determined. The experiment lasted over 12 days, during the last six of which the excrements were carefully collected and analysed.

The first pair of pigs, Nos. 1 and 2, were fed for some days on barley-meal, and then No. 1 was killed, cut up, and analysed. No. 2 was fed for four months on barley-meal of three sorts, and weighed regularly. Three determinations of the digestive coefficient of the meal were made with the following results:—

Barley.	A.		B.		C.	
	Percentage contained.	Percentage of this digested.	Percentage contained.	Percentage of this digested.	Percentage contained.	Percentage of this digested.
Albumin ..	14·44	82·94	11·62	77·94	10·87	75·47
Fat .....	1·60	61·73	1·21	46·03	1·51	68·49

With the aid of the above figures, the total amounts of albumin and fat digested during the whole time of the experiments were calculated. At the end of four months, the animal was killed, cut up, and after well mixing, samples of the various parts were analysed.

The second pair were treated, at first, as above, then No. 3 was killed, and No. 4 fed for four months; barley alone was given at first, and then a mixture of barley with gradually increasing proportions of starch and sugar, almost equal quantities of the former two being given towards the end. Three experiments were also made to determine the digestive coefficients of the barley, and a considerable depreciation was observed as the quantity of starch increased, the numbers in the last experiment being albumin 55·4 and fat 17·5 per cent., assuming the whole of the starch and sugar to have been digested. At the end of four months No. 4 was killed.

Analyses of the carcasses of the four animals gave the following results in grams:—

	No. 1.	No. 2.	No. 3.	No. 4.
Fat .....	957	9264	1009	6439
Albumin ..	687	2516	1478	2671

No. 2 had therefore gained during the experiment 8576 grams fat and 1559 albumin, whilst the quantities digested had been only 655 grams fat and 7493 albumin: allowing that the excess of albumin had all been converted into fat, this still leaves a very large quantity of fat gained to be accounted for. In the case of pig No. 4 the

same fact was also observed: and even admitting the very improbable contingency that the whole of the albumin given had been digested, there was still a considerable margin left, showing that the fat must have also been derived from other sources. That the carbohydrates therefore participate in the formation of fat in the organism is a necessary inference from the above experiments. J. K. C.

**Effect of Exhausted Beetroot Pulp on Cows' Milk.** By A. ANDOUARD and V. DÉZAUNAY (*Compt. rend.*, 97, 809—811).—It is generally believed that beetroot pulp from which the sugar has been extracted by diffusion, constitutes a valuable food for cattle. Experiments made by the authors show that when a cow is fed with pulp which has been kept in silos, the yield of milk increases by nearly 32 per cent. of its original amount; the proportion of casein and inorganic salts is not sensibly affected, but the proportion of fat increases by 12.4 per cent., and that of sugar by 23.64 per cent. of its original amount. The milk, however, has a less agreeable taste, and shows a decided tendency to acid fermentation. Moreover, it was found to be unsuitable for the nourishment of infants.

This alteration in the character of the milk is most probably due to the acids in the exhausted pulp. The pulp used in these experiments contained an amount of organic acid equivalent to 1.08 per cent. of acetic acid, and consequently a cow consuming 50 kilos. of pulp per day (an average quantity) would absorb 540 grams of acetic acid and its homologues. C. H. B.

**Partially Oxidised Sulphur in Urine.** By R. LÉPINE and G. GUÉRIN (*Compt. rend.*, 97, 1074—1076).—The incompletely oxidised sulphur in urine cannot all be oxidised by chlorine or bromine; it is completely oxidised only by fusion with potassium nitrate and hydroxide. The unoxidised sulphur may therefore be divided into two portions, *sulphur easily oxidised*, and *sulphur difficult to oxidise*. The sulphur derived from the bile is included in the latter portion, as might have been expected from the known stability of taurine and its derivatives. This conclusion was confirmed by a number of experiments with dogs, in which the amount of bile reabsorbed was increased, the result being that the amount of sulphur difficult to oxidise in the urine was also increased. Some of the sulphur difficult to oxidise is, however, derived from some source other than the bile. A dog with a complete biliary fistula was kept sometimes on soup diet (bread and fat), sometimes on a diet of horseflesh. In the first case, the sulphur oxidised with difficulty was 30 per cent. of the total sulphur; in the second case, it was 23 per cent. If the amount of nitrogen in the urine is taken as 100, then the sulphur oxidised with difficulty was equal to 1.8 in the first case, and 0.8 in the second. Numerous experiments show that the urine contains a large proportion of sulphur difficult to oxidise, in many pathological conditions in which there is no reason to suppose that the amount of bile reabsorbed is in any way increased. C. H. B.

**Hydrocyanic Acid from Animals.** By M. WEBER (*Bied. Centr.*, 1883, 565).—It has been shown chemically by G. Geldensteen that certain *Fontaria* possess glands capable of secreting free hydrocyanic acid. J. T.

**Stony Concretions in Animals.** By F. SCHUBERG (*Bied. Centr.*, 1883, 565).—The author confirms the view that the introduction of foreign matter induces the formation of intestinal stones. He gives analyses of three stones: (1) given by Abeles, (2) from the *Procesus vermiformis* of a man, and (3) from the *Intestinum rectum* of a boy:—

	(1.)	(2.)	(3.)
Water .....	22.0	57.3	—
Ammonia-magnesium phosphate	—	24.4	63.9
Calcium phosphate .....	60.5	6.7	23.8
Magnesium phosphate .....	4.3	—	—
Calcium carbonate .....	—	—	4.6
Calcium sulphate .....	1.1	1.3	0.7
Alcohol-ether extract .....	0.3	0.8	0.8
Other organic matter .....	11.3	9.2	6.0

Stones from plant-eating animals often contain calcium carbonate.

J. T.

**Connection between Chemical Constitution and Physiological Action.** By T. L. BRUNTON and J. T. CASH (*Proc. Roy. Soc.*, 35, 324—328).—This paper contains a series of investigations on the physiological action of the salts of ammonium, the amines, the alkali metals, and the alkaline earths.

All the ammonium salts affect the spinal cord, motor nerves, and muscles, and tend ultimately to poison these structures, but the course varies with the salt employed. Ammonium bromide, and the sulphate, phosphate, and iodide to a less degree, cause coagulation of the stroma of the red blood-corpuscles. The amines and their salts affect the spinal cord, motor nerves, and muscles, and their action differs most markedly from that of the ammonium salts; the former cause tetanus, the latter motor paralysis. The irritability of the muscle is increased by the hydrochlorides, but their contractile power is less affected by them, more than by the sulphates, and most by the hydriodides. Of the salts of methyl-, ethyl-, and amyl-ammonium, the primary are more active than either the secondary or tertiary, but the tetrasubstituted compounds are the most active.

The chlorides of the alkali-metals differ from ammonia in having very little tendency to stimulate the spinal cord; the chief symptom of poisoning produced by them is increasing torpor. The contractile power of muscles is increased by rubidium, potassium, and cæsium, unaffected by sodium, and invariably diminished by lithium.

The alkaline earths, as regards their action on the nervous system, may be divided into two groups: (a), beryllium, calcium, barium and strontium; (b), yttrium, didymium, erbium and lanthanum. Group a has a tendency to increase reflex action, group b to paralyse motor centres. The contractile power of muscles is increased by barium.

erbium, and lanthanum, diminished by yttrium and calcium. Contraction is increased by barium, calcium, yttrium, and beryllium; that produced by barium is enormous, resembling the effect of veratria.

The alteration effected on muscle by one substance may be neutralised, but not increased, by another substance having a similar action. Potassium shortens the lengthened curves of barium, calcium, strontium, and lithium; the veratria-like curve of barium is counteracted by almost all the substances, producing a shorter curve than itself.

Some relations are pointed out between the atomic weights of antagonising elements, but the data are too limited to admit of any generalisation.

By alternate application of acids and alkalis, the muscles of a frog describe on a slowly revolving cylinder curves resembling those described by the normal contraction of a muscle on stimulation.

The lethal activity on frogs of the chlorides of the metals of the alkali and alkaline salt-group was also the subject of investigation; potassium chloride is the most, and calcium chloride the least powerful.

V. H. V.

**Cholera.** By R. DE LUNA (*Compt. rend.*, **97**, 633).—The cause of cholera always exists in the air, and is transmitted by persons and things. It acts exclusively through the organs of respiration, and incubation generally takes place when the individual is in a passive condition, and particularly during sleep. The microbe or ferment acts especially on the blood corpuscles and prevents hematosis, producing a kind of gradual asphyxia. According to the experience of the author and of Spanish physicians, the only means of saving infected patients in the stage of chills is the careful inhalation of oxides of nitrogen mixed with air. The effect is very rapid, two or three inhalations being sufficient to place the patient out of danger in a few hours. As a precaution against the disease, rooms, vessels, &c., should be fumigated with the nitrogen oxides twice a day—on retiring and after rising.

C. H. B.

**Distribution of Arsenic in a Human Body.** By R. H. CHITTENDEN (*Amer. Chem. J.*, **5**, 8—14).—In a case of suspected poisoning by arsenic, the internal organs were removed and analysed soon after death; about six months later the body was exhumed, and about one half of the entire muscle and bony tissue removed for further examination in order to ascertain the distribution and entire amount of arsenic in the body.

Such of the internal organs as had been placed in alcohol were ground to a thick paste with the alcohol in a mortar and weighed portions then taken for analysis. The muscle and bony tissues were dissolved in nitric acid at a gentle heat, and portions of this liquid then used for the determinations.

The arsenic was estimated by the process previously described by the author (*Abstr.*, 1881, 648). The figures given are those calculated on the entire organs, &c., from the (generally duplicate) results so obtained:—

	Grain $\text{As}_2\text{O}_3$ .
Stomach and œsophagus .....	0.158
Liver .....	0.218
Intestines .....	0.314
Kidneys .....	0.029
Heart .....	0.112
Lungs and spleen .....	0.1719
Brain .....	0.075
Trachea, larynx, and tongue .....	0.081
Diaphragm.....	0.010
Left arm (weight, $43\frac{1}{4}$ oz.) .....	0.094
Right leg, except thigh bone (weight, 164 oz.) ....	0.118
Thigh bone (weight, $7\frac{1}{2}$ oz.) .....	—
Transverse section of body at pelvis, including pelvic bones (weight, $143\frac{1}{2}$ oz.) .....	0.186
Muscle from breast (weight, $18\frac{1}{4}$ oz.) .....	0.098
Muscle from back (weight, 24 oz.).....	0.356

The entire body would therefore contain about 3.1 grains of  $\text{As}_2\text{O}_3$ . In the author's opinion there is a marked difference in the distribution of arsenic in the muscular tissue according to whether the poison has been administered in a single dose, when the distribution is very irregular, or in long-continued small doses, when the regular distribution of the arsenic is very noticeable.

A. J. G.

**Colorado Beetle.** By J. D. FORBES (*Arch. Pharm.* [3], 21, 314).—The author has examined the Colorado beetle, *Doryphora decemlineata*, for a vesicating substance. No distinct evidence of such a constituent could be obtained when the live beetles were crushed in a mortar, extracted with various solvents, and the residues from the latter examined. After killing the beetles with ether, drying, powdering, and exhausting with chloroform, a dark oil was obtained by the chloroform extract which had marked vesicating properties.

W. R. D.



## Chemistry of Vegetable Physiology and Agriculture.

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**Reduction of Nitrates by Ferments.** By A. SPRINGER (*Amer. Chem. J.*, **4**, 452—453).—According to the author, the roots of plants are covered with small organisms which reduce nitrates, with evolution of nitric oxide. This ferment closely resembles the butyric ferment, and is probably identical with the *Microzyma cretæ* of Bechamp; it is composed of small cylindrical rods rounded at the extremities, generally isolated, but sometimes joined two by two. They move rapidly with a wriggling motion, and often bend their bodies until

they form a perfect circle. Another ferment or modification is somewhat smaller, and spins round its smaller diameter as an axis. Phenol has no appreciable action on the new ferment. Similar results have been obtained since the author first announced his results, by Gayon and Dupetit (*Abstr.*, 1883, 229), and Déhéraïn and Maquenne (*ibid.*, 230). A. J. G.

### Fermentation of Cane-Sugar in Contact with Arable Soil.

By P. P. DÉHÉRAÏN and MAQUENNE (*Compt. rend.*, 97, 803—805).—When cane-sugar is mixed with arable soil, chalk, and water, and the mixture kept at 35—40° for a considerable time, the whole of the sugar disappears. The gas which is given off at first is almost pure hydrogen, but as fermentation proceeds the proportion of carbonic anhydride becomes greater and greater. The other products of the fermentation are small quantities of ethyl alcohol, and still smaller quantities of higher alcohols of the same series; acetic and butyric acids, together equal in amount to about half the weight of the sugar, and a smaller quantity of propionic acid, but no acid higher than butyric. These facts show that the ferment existing in arable soil belongs to the class of butyric ferments. C. H. B.

### Comparative Poisonous Action of Metals on Bacteria.

By C. RICHET (*Compt. rend.*, 97, 1004—1006).—The liquid employed was a mixture of 900 grams sea-water, 100 grams neutralised urine, and 1 gram commercial peptone, and the particular metal was added in gradually increasing quantity in the form of chloride until no bacteria were developed after 48 hours at 16—20°. In the following table column A gives the minimum quantity of each metal per litre which will prevent the development of bacteria after 48 hours, and column B gives the minimum quantity of each metal per litre which will kill marine fishes in 48 hours.

	A.	B.
Mercury (Hg <sup>''</sup> ) ....	0·0055 gram.	0·00029 gram.
Zinc .....	0·026    "	0·0084    "
Cadmium .....	0·040    "	0·017    "
Copper (Cu <sup>''</sup> ) ....	0·062    "	0·0033    "
Nickel .....	0·018    "	0·125    "
Iron (Fe <sup>'''</sup> ) .....	0·24    "	0·014    "
Barium .....	3·35    "	0·78    "
Lithium .....	6·9    "	0·30    "
Magnesium .....	7·2    "	1·50    "
Manganese .....	7·7    "	0·30    "
Ammonium .....	18·7    "	0·064    "
Calcium .....	30·0    "	2·40    "
Sodium.....	43·0    "	24·00    "
Potassium.....	58·0    "	0·10    "

The amount of each metal which will kill fish is always much less than that required to prevent the development of bacteria. The marked poisonous action of ammonium, lithium, and potassium on

fish and all animals is in striking contrast to the slight effect which these metals exert on plants and bacteria. Poisons may be divided into two classes, viz., general poisons, of which mercury is the most perfect, which even in small quantities have a deleterious action on both plants and animals; and special poisons, such as potassium and ammonium salts and the alkaloids, which are injurious only to animals, and exert little or no poisonous action on plants. The difference is probably due to the fact that poisons of the second class act only on nerve cells, whereas those of the first class act on all cells. Possibly the action of ammonium and potassium salts may serve to distinguish between plants and animals in the lower forms of life.

C. H. B.

**Distribution of Water in Heliotropically inclined Parts of Plants.** By A. THADE (*Bied. Centr.*, 1883, 568).—Kraus has found, amongst other results, that in positive heliotropically inclined organs, the shady side contains more water than the light side. The author found from 12 experiments a difference of 0.004 per cent. only. Normal growing plants similarly examined gave a difference of 0.115 per cent. as the average of six experiments. The author shows that different ways of treating the plant give considerable differences in the amount of water found.

J. T.

**Plants from Seeds of Various Sizes.** By HELLRIGEL (*Bied. Centr.*, 1883, 530—542).—The magnitude and development of the embryo, and the reserve stock of nutriment in seed, may be assumed to be closely related to the size of the seed in cases where the latter has not a complicated envelope.

*Influence of the Absolute Weight of Seeds.*—Grains of barley having a sp. gr. between 1.19 and 1.2 were divided into four groups, according to weight, and sown. The development of the heavier seeds proceeded more quickly at first, but in course of time the weight of the plants produced became nearly equal.

*Influence of Specific Gravity.*—Experiments with barley seeds of varying sp. gr. showed that differences in this respect produced no difference in the plant.

*Influence of Relative Ripeness.*—Rye seeds reaped at five different stages of growth were used for experiment. I. Cut when grain and straw were still green, the former very small, with clear watery sap. II. Straw still green, grain strongly grown, sap milky. III. Straw becoming yellow, grain full size but still green, and very soft. IV. Straw yellow and tolerably dry, grain hard, no sap (said to be yellow-ripe). V. Straw and grain dry, the latter easily removable (said to be over-ripe or dead-ripe). Each group was divided into four classes:—*a.* The seeds were carefully separated from the plant—after-ripening thus prevented. *b.* The ears were cut off and bundled—restricted after-ripening. *c.* Stalks cut some inches above the ground as in ordinary reaping. *d.* The whole plant was taken up and placed in distilled water, the most favourable condition for after-ripening. The seeds were sown partly in vessels and partly in the open ground. The soil consisted of rich garden mould and poor sandy ground. The following results were obtained:—In poor soil, the unripe seeds were

exceedingly backward; part did not germinate, and part remained weakly all through life. In rich soil, however, the backwardness was much less marked, and was mostly shown by the non-germination of some of the seeds; the plants, although weak at first, became completely developed. The after-ripening of the seed, when left for a time in contact with the remaining parts of the plant, has a decidedly favourable influence on the germinating power of the seed, but much less in increasing the producing power of the resulting plant.

Experiments with potatoes showed that large potatoes give the best yield, which is opposed to common practice, where moderate sized ones are chosen. The sp. gr. of the potato appears to have no influence on the yield.

J. T.

**Mineral Constituents of the Seeds of Forest Trees.** By R. HORNBERGER (*Landw. Versuchs.-Stat.*, 29, 281—289).—The author has analysed the ash of seeds of elm, ash, hornbeam, maple, birch, pine, and larch. The seeds were obtained from dealers, having been gathered in the most various localities, and representing therefore an average material. They were incinerated, and the ash constituents determined according to well-known methods. The following results were obtained:—

	Ash per cent	In 100 parts ash.								
		K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> .	Mn <sub>3</sub> O <sub>4</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	SiO <sub>2</sub> .
Elm.....	9·30	32·29	0·62	23·73	6·27	3·24	0·32	11·22	4·86	13·94
Ash.....	4·24	44·18	0·85	21·77	6·57	0·89	0·09	15·21	9·06	1·29
Hornbeam	2·4~	25·15	0·92	35·62	7·82	5·69	2·64	14·28	3·93	5·05
Maple....	6·79	37·37	0·84	27·66	5·82	2·94	2·49	14·16	5·27	6·18
Birch....	4·20	27·03	1·38	23·77	9·20	8·91	2·73	10·89	4·80	8·94
Pine.....	4·28	24·02	0·72	1·63	14·22	2·10	2·05	37·77	4·45	16·00
Larch....	2·07	34·68	1·25	2·41	12·81	1·30	1·83	34·15	4·09	5·88

The most striking feature in the above table is the great difference in the lime contained in the seeds of the pine series and in those of the other trees. Whilst the former contain less than 2½ per cent., the latter contain from 20 to 35 per cent. of lime; on the other hand, the pine seeds are very much richer in magnesia and phosphoric acid. The large quantity of silica in the seeds of the pine and elm seems to stand in some connection with the fact noticed by previous observers that the woods of these trees take up large quantities of silica.

J. K. C.

**Constituents of the Larch Fungus.** By E. JAHNS (*Arch. Pharm.* [3], 21, 260—271).—Although the larch agaric (*Polyporus officinalis*) has been investigated by more than one chemist, conflicting statements concerning its constituents still exist. The author, with the view of clearing up the question, has re-investigated this

plant. By extraction with hot strong alcohol it yielded about 18 per cent. of a crystalline acid melting at about  $139^{\circ}$ , and easily soluble in alcohol, glacial acetic acid, and turpentine, less soluble in ether, and nearly insoluble in chloroform, benzene, and cold water. The acid is dibasic, forming normal salts with the alkali metals, which are easily soluble in water, and acid salts which are only slightly soluble: with the majority of the metals, it forms insoluble salts, which are precipitated in the amorphous state from aqueous solutions. Analysis showed that *agaricic acid* was a homologue of malic acid, represented by the formula  $C_{16}H_{30}O_5 \cdot H_2O$ . On oxidation with nitric acid, it is converted into succinic and butyric acids. The principal salts are described in the paper. This acid is identical with the "agaricic acid" of Fleury, the "laricin" of Martius; and the substances named by Schoonbroodt "agaricin" and "pseudo-wax" by Trommsdorff, are probably the same acid in an impure state. The original alcoholic extract of the fungus also yields a substance which crystallises in needles from a solution in absolute alcohol. It is insoluble in water, and nearly so in ether, chloroform, and cold alcohol, but dissolves in potash solution. It melts at about  $272^{\circ}$ , and sublimes in white needles. This substance, which is probably an alcohol, exists to the extent of about 5 per cent. in the plant. The alcoholic mother-liquors from this substance contain a white amorphous body, which is deposited in a colloidal form from its solution in chloroform. It appears to be an acid, and occurs to the extent of about 4 per cent. in the fungus. Finally a red amorphous resin was obtained from the original alcoholic extract, in which it was very soluble. This is the bitter purgative constituent of the fungus, and is present to the extent of about 30 per cent.

W. R. D.

**Paraguay Tea.** By A. W. SELLIN (*Arch. Pharm.* [3], 21, 292).—This substance, which is also known as *maté*, is yielded by the *Ilex paraguayensis*, which grows in the highlands of Southern Brazil, the Argentine Republic, and Paraguay. The leaves are gathered in the spring, dried at a low temperature, and packed. An infusion of it is drunk by the South Americans in the place of tea.

W. R. D.

**Glycogen in Plants.** By ERRERA (*Biol. Centr.*, 1883, 355).—Glycogen has been detected in *Ascomycetes pilobolus*, &c., and also in plants of a higher order, as *Solanum*, *Linum*, &c. A compound analogous to dextrin is found in *Solanum* and *Agaricus*, but not in *Peziza* or *Lemanea*. Glycogen may as a rule be readily detected in plants by the micro-chemical method, when it exhibits all the properties possessed by this compound as obtained from the animals.

E. W. P.

**Minjak-Lagam Balsam.** By G. HAUSSNER (*Arch. Pharm.* [3], 21, 241—256).—Minjak-Lagam, a balsam resembling copaiba, but the botanical origin of which is unknown, has been chemically examined by the author. On distillation with water, it yielded one-third of its weight of an essential oil of sp. gr. 0.928 at  $15^{\circ}$ , and similar to the essential oil yielded by copaiba and gungun balsams. The analysis and vapour-density determination correspond with the formula

$C_{20}H_{32}$ , and it yields a crystalline hydrochloride,  $C_{20}H_{32} \cdot 4HCl$ , melting at  $114^{\circ}$ . The resin remaining in the retort after the distillation of the oil, contained an amorphous acid which formed uncrystallisable salts with many of the metals. The copper salt, on analysis, gave figures pointing to the formula  $C_7H_{12}O_3Cu$ . The resin when fused with potash, heated with acid and ether in the usual way, and the extract distilled with water, yields butyric acid, whilst a substance remains in the solution which appears to be an acid derived from benzene, as it gives a violet colour with ferric chloride. Minjak-Lagam balsam therefore resembles gurgum balsam in many of its characters, and probably has a similar botanical origin, namely, a species of *Dipterocarpus*. It appears to differ from this balsam in yielding an uncrystallisable resin acid which has a lower molecular weight than the resin acid of gurgum. It is probably further distinguished by the fact that its resin yields an aromatic acid as well as butyric acid when fused with potassium hydroxide. W. R. D.

**Phylloxera.** By T. TOZZETTI and others (*Bied. Centr.*, 1883, 547—551).—According to Henneguy this pest has considerably increased in the vineyards in the district of Béziers, where carbon bisulphide has not been employed. P. Mouillefert states that potassium thiocarbonate is being applied to the vineyards of Médoc and the south of France. Culeron has applied the same substance for more than five years with good results, and has made many comparative experiments on the subject. He recommends the application to be made from October to April. J. T.

**Indian Wheat.** By BALLAND (*Compt. rend.*, 97, 805).—Indian wheat contains a relatively considerable quantity of seeds of *leguminosæ* and some other plants. Wheat shipped at Bombay was found to contain seeds of *Vicia peregrina*; *Cicer arietinum*; *C. arietinum*, var. *nigrum*; *Ervum uniflorum*; *Cajanus indicus*; *Acacia lubeck*; *Tamarindus indica*; *Cassia* (?); *Rhynchosia* (?); *Citrullus vulgaris*; *Ricinus communis*; *Linien usitatissimum*. C. H. B.

**Maize as Food for Horses.** By GERSSDORFF (*Bied. Centr.*, 1883, 566).—7·5 to 9 kilos. per head per day, mixed with chaff and followed by good hay, kept the animals in as good condition as 10 kilos. oats. J. T.

**Fermenting Maize for Milch Cows.** (*Bied. Centr.*, 1883, 567.)—The cows were previously fed on mangel-wurzel; gradually this was diminished to one-half, and replaced by maize fermented in pits. The amount of milk and butter obtained remained the same; but the latter was somewhat whiter than before. There was no apparent change in the bulk of the animal. J. T.

**Palm-oil Residue as Fodder.** By MÄRCKER (*Bied. Centr.*, 1883, 566).—The author gives three analyses of palm-kernel-meal, (1) after being stored three weeks; (2) nine months; and (3) quite fresh:—

	(1.)	(2.)	(3.)
Water .....	9.16	9.75	9.43
Ash .....	5.68	3.93	3.56
Protein.....	12.31	15.13	15.31
Cellulose .....	23.27	25.27	21.20
Nitrogenous matter (extractive).	44.91	41.23	43.46
Fat .....	4.67	4.56	7.04

The author combats the view that this is not a good milk-fodder, and asserts that the most important constituents for milk production are the nitrogenous substances and not the fat. J. T.

**Earth-nut Cake.** By HOLDEFLEISS (*Bied. Centr.*, 1883, 526—528).—This cattle food having given unsatisfactory results of late, although numerous analyses show 40 to 50 per cent. protein, and several per cent. albumin, with other food constituents normal, it was microscopically examined, and in many cases was found to contain quantities of fungus spores. 48 to 60 hours after moistening with very little water, the meal becomes covered with a yellow coating of an *Aspergillus*, similar to *Aspergillus flavus*. This fungus is of special interest, as in Japan it induces the fermentation and formation of sugar in rice. In the presence of more moisture, a black *Aspergillus* appears in colonies, also a thick covering of mucor-like fungi. These fungi cause changes in the meal, primarily a disappearance of albumin. Enormous quantities of bacteria were observed in many samples. J. T.

**Composition of Beetroot.** By PAGNOUL (*Bied. Centr.*, 1883, 570).—The author gives analyses of beetroot—(1) grown in soil excessively manured with stable dung, and (2) grown in soil ordinarily manured with an artificial manure containing Chili nitre:—

	(1.)	(2.)
Weight of the root.....	820 g.	492 g.
Sugar .....	13.51 p. c.	4.42 p. c.
Alkalis.....	0.40 „	1.07 „
Nitrate.....	0.04 „	0.73 „
Salt, per 100 sugar.....	2.27 „	24.12 „
Nitrate „ .....	0.31 „	16.47 „

J. T.

**Sugar Beet.** By G. MAREK (*Bied. Centr.*, 1883, 543—547).—The author took varieties richest in sugar to ascertain the connection, if any, between the absolute and sp. gr. of portions, and the yield in sugar. Generally the sp. gr. of the whole root is less than that of parts of the root. Of the parts of the root, the point is the heaviest, next the middle part or body, then a side piece of the body, and lastly the head. The author is of opinion that weighing the whole root gives better results than judging by appearances; and that weighing various portions of the root is advisable in selecting for seeding; for this purpose a portion from the side of middle part is most suitable to weigh, in order to separate light from heavy roots. The sap from

the various portions gave over all a higher sp. gr. than the root itself. Sap from the middle portion was the heaviest; then followed the root, and last the top. Sap from a number of roots generally gives higher rotation with a higher sp. gr., but this is not invariable. Of the parts of the same root, sap from the middle part gave the highest rotation, next from the side piece of the middle; then point, and lastly that of the head. Beets with rosette-like arrangement of leaves were found to be richer than those with a more vertical arrangement. The author shows that the so-called "*aufschussrüben*" as compared with normal plants have a lighter sap, less sugar, and lighter root, with a greater weight of leaves and head. When the seed-shoots of such plants are removed beforehand, the roots become still poorer in sugar, and richer in salts and cellulose. The increased amount of cellulose interferes prejudicially with the extraction of the sugar.

J. T.

**Soil Temperature in Relation to the Air Temperature.** By W. HOSSFELD (*Bied. Centr.*, 1883, 562).—Observations, made daily during the first six months of this year, showed that in a clay soil at Kranichfeld the temperature increased from the surface downwards to a depth of 2 meters until March 12; after this the temperature diminished from the surface downwards. The observations were made at 8 A.M.

J. T.

**Irrigation as Preventive of Injury from Frost.** By T. v. NEERGARD (*Bied. Centr.*, 1883, 561).—The injurious action of night frost on grass, &c., in spring can be prevented by covering the meadows with 4—6 cm. of water; this practice should be continued until the end of May, until the frost has entirely disappeared.

J. T.

**Nitric Acid in Soils and Subsoils at Rothamsted.** By Sir J. B. LAWES, J. H. GILBERT, and R. WARINGTON (*Jour. Roy. Agri. Soc.*, 1883, 331).—The unmanured and uncropped soils of the three drainages have yielded drainage waters containing on an average of six years 40.2 lbs. of nitric nitrogen per acre. This amount must be below the annual produce of good soil. Nitric acid was determined in many soils: the samples were taken by driving a rectangular iron tube, 6 inches square and 9 inches deep, into the ground, removing the contents as a sample, and again driving the tube down to obtain samples of the succeeding depths: the soils were at once broken up and dried at 55°. The nitric acid was determined by a modification of Schloesing's method (*Trans.*, 1882, 345—351). The immediate drying of the soil is indispensable, otherwise the results are too high.

*Fallow Soils.*—Three soils in fair condition, cultivated as bare fallow, contained at the end of summer 56.5—59.9 lbs. of nitric nitrogen per acre to a depth of 27 inches. Estimating as far as possible the preceding loss of nitrate by drainage, it would appear that about 80 lbs. of nitric nitrogen per acre were produced during the season (15 months) of fallow. Land in poor condition contained much less nitrate. When the preceding summer had been dry, the nitrate was chiefly near the surface.



*Soils growing Cereal Crops.*—Where no excess of nitrogenous manure is employed, very small quantities of nitrate are found in the soil during summer, owing to assimilation by the crop. If rain occurs after harvest, and especially if the land is ploughed, considerable formation of nitrate takes place. Nitrate continues to be present through the winter, notwithstanding loss by drainage, slow production being always in progress. In late spring or early summer, the nitrate again disappears if the land is under crop.

Determinations of nitric acid were made in the soils of the experimental wheat field, taken October, 1881. Much rain had fallen since harvest, and the land had been ploughed; conditions were thus favourable to nitrification. Plots permanently unmanured contained 15.0—17.9 lbs. of nitric nitrogen per acre to a depth of 27 inches. Plots receiving ash-constituents alone, 21.2 to 24.3 lbs. Plots receiving ash-constituents, with 400 lbs. of ammonium salts or 550 lbs. nitrate of sodium the preceding spring, contained 24.6—39.8 lbs. Plots with the above-mentioned nitrogenous manure alone, 28.3—54.1 lbs. With 1700 lbs. of rape cake, 34.2 lbs. With 14 tons of farmyard manure, 52.2 lbs. The last two manures were applied the preceding autumn. On plots receiving no nitrogenous manure, or not excessive quantities of ammonia or nitrate, the nitrate found was due to nitrification of crop and weed residues and of the humic matters of the soil; the quantity of nitrate generally bore a distinct relation to the quantity of the preceding crops. Where an excess of nitrate of sodium had been applied, a considerable residue of the manure was found in the subsoil. Where rape cake or farmyard manure was used, the nitrate was partly derived from the nitrification of residues of manure. The nitrogen of permanently unmanured soil nitrifies with more difficulty than the nitrogen of soil which has yielded large crops, or than nitrogenous residues of rape cake or farmyard manure.

The soils of the experimental barley field were sampled in March, 1882, to the depth of 27 inches. The permanently unmanured land contained 15.7 lbs. of nitric nitrogen per acre. That receiving ash-constituents alone, a mean of 20.1 lbs. That receiving 200 lbs. ammonium salts, or 275 lbs. nitrate of sodium, with or without ash-constituents, a mean of 23.3 lbs. Plots receiving 1000 lbs. rape cake, with or without ash-constituents, a mean of 30.1 lbs. The plot receiving 14 tons farmyard manure, 44.1 lbs. The washing of the autumn and winter rains had tended to equalise the amounts of nitrate. The influence of crop residues is not so marked as in the wheat field, barley leaving a smaller residue in the soil than wheat.

*Soils growing Leguminous Crops.*—The nitrate in soils that have grown beans or clover is much smaller than that found in similar uncropped soils. Although leguminous crops thus assimilate nitric nitrogen, the total quantity of nitrogen found in such crops often greatly exceeds the quantity of nitric nitrogen at present recognised as occurring in soils. We must thus apparently assume for leguminous crops a further source of nitrogen; in the case of cereal crops, the nitric nitrogen of the soil appears to furnish an adequate supply.

Few determinations of nitric nitrogen have yet been made for

depths below 27 inches; in most cases only small quantities were found. It is a question whether the nitrates in a clay subsoil are not destroyed by reduction.

R. W.

**Yield of Crops under Steam Cultivation.** By M. MÄRCKER (*Bied. Centr.*, 1883, 508—511).—Experience with Fowler's steam ploughs during the period 1872—80 leads to the following conclusions:—

Against hail, frost, rust, and the depredations of animals, &c., it has no advantage over animal cultivation; but in very wet or very dry seasons it greatly reduces the injurious results of such abnormal weather. In dry weather, the plants can more readily get deeper in search of moisture, whilst in wet seasons the excess water more readily drains away into the subsoil. Another essential advantage is the immediate destruction of weeds. Further, the after cultivation of the crop is facilitated. From figures given the wheat crops averaged 19·4 per cent. better; barley, 32·1 per cent.; oats, 1·2 per cent.; maize, 12·5 per cent., and beet, 26·8 per cent. The wheat crops compared were six years before and six after the introduction of steam cultivation, the other crops were nine years before and nine after.

J. T.

**Coexistence of Ammonium Carbonate and Potassium Sulphate in Guano.** By E. CHEVREUL (*Compt. rend.*, 97, 786—787).—Guano not unfrequently contains compact homogeneous moist snow-white masses consisting of ammonium subcarbonate, associated with potassium sulphate and water.

C. H. B.

**The Guano of Cape Vert.** By A. ANDOUARD (*Compt. rend.*, 97, 858—859).—The guano is mixed with a considerable quantity of stones. When these are removed it has the composition:—

Moisture.....	15·21
Organic nitrogen .....	0·28
Nitrogen as ammonia .....	0·04
Organic matter .....	10·63
Phosphoric acid.....	11·37
Lime, magnesia, and ferric oxide .....	20·49
Salts soluble in water .....	0·92
Silica and silicates.....	41·06
	<hr/>
	100·00

C. H. B.

**Nitrogen in Bone-meal.** By WAGNER (*Bied. Centr.*, 1883, 563).—Commercial bone-meal contains 1 to 4 per cent. of nitrogen, on an average 3·2 per cent. This variation in amount depends on the previous treatment to which the bone has been subjected for the extraction of its fat. Hence it is advisable to extract the fat by means of solvents such as petroleum. Bones so treated contained  $4\frac{1}{2}$  to 5 per cent. of nitrogen, and consequently have an increased value.

J. T.

**Weathering of Bone Manure.** By J. KÖNIG (*Bied. Centr.*, 1883, 562).—Steamed bone-meal mixed with stable dung spread on a field in the spring of 1883 had quite disappeared at the present time, whilst in another case raw fragments of bone can be found which was applied along with stable dung from two to four years ago. Such bone fragments washed and analysed gave, after two, three, and four years on the soil respectively—of nitrogen, 1·1, 0·7, and 0·4 per cent. respectively; of phosphoric acid, 10·1, 0·7, and 0·3 per cent. respectively; and of calcium carbonate, 41·2, 49·1, and 42·7 respectively. Hence raw bone takes at least four years to weather completely.

J. T.

**Influence of Superphosphates on the Quality of the Yield.** By F. FARSKY (*Bied. Centr.*, 1883, 511—512).—The author had opportunity during some manure experiments of comparing the effects of Chili nitre and superphosphate on buckwheat. His results show (1) that superphosphate induces early maturity in the plant, and (2) that it also increases the absolute and relative weight of the seeds. Further Chili nitre retards the harvest, and in no instance produces heavier seeds.

J. T.

**Phosphate from the Rata Island.** (*Bied. Centr.*, 1883, 562).—The material has been repeatedly analysed in England; it contains:—

	Analyst.				
	1. A. Voelcker.	2. W. A. Carry.	3. E. Redwood.	4. At the Mint.	5. At the Mint.
H <sub>2</sub> O.....	2·63	} 11·20	8·23	10·92	10·00
Organic matter (and comb. H <sub>2</sub> O) ....	7·53				
P <sub>2</sub> O <sub>5</sub> .....	28·18	32·36	27·60	28·03	26·50
CaO .....	30·45	26·88	37·63	32·08	30·60
Fe <sub>2</sub> O <sub>3</sub> .....	10·85	} 21·60	{ 9·43	7·42	9·56
Al <sub>2</sub> O <sub>3</sub> .....	11·99			9·44	11·22
MgO .....	1·73	—	—	—	—
Na <sub>2</sub> O .....	—	—	—	0·51	} 1·37
K <sub>2</sub> O .....	—	—	—	trace	
SiO <sub>2</sub> .....	0·25	—	—	—	trace
CO <sub>2</sub> .....	1·35	1·26	1·84	3·30	3·25
Insol. (silicate).....	5·04	6·40	5·19	7·86	7·50
	100·00	100·00	100·00	100·00	100·00

The insoluble (in nitric acid) residue of No. 4 gave 1·11 per cent. TiO<sub>2</sub>, 1·97 of SiO<sub>2</sub>, 1 of Al<sub>2</sub>O<sub>3</sub>, and 3·78 of Fe<sub>2</sub>O<sub>3</sub>. Also in the same sample traces of ammonia were found.

J. T.

**Compost Manure.** By A. MAYER (*Bied. Centr.*, 1883, 564).—Amsterdam compost manure is richer in phosphoric acid and nitrogen than in former years.

	Organic matter.	Nitrogen.	Ash.	Phosphoric acid.	Potash.	Water.
Amsterdam, Jan. 16, 1882 .....	17·0	0·7	21·5	0·7	0·4	61·5
Amsterdam, Jan. 11, 1880 .....	11·8	0·3	42·2	0·3	0·4	46·0
Groningen compost ...	13·7	0·8	22·7	0·6	2·2	63·6

J. T.

**Effect of Potassium and Sodium Nitrates on the Growth of Potatoes.** By P. P. DÉHÉRAIN (*Compt. rend.*, **97**, 998—1000).—Two pieces of land were sown with potatoes; one was manured with potassium nitrate, and the other with an equal quantity of sodium nitrate, the quantity applied being equivalent to 400 kilos. per hectare. In both cases the average yield was the same, viz., 805 grams per root, a yield considerably in excess of that obtained under ordinary conditions. The influence of the nitrates is very considerable, but the nature of the base does not seem to affect the results. The potatoes manured with sodium nitrate, or with other salts of sodium, contain only potassium and no sodium. It would appear therefore that the sodium salts applied as manure decompose the potassium compounds in the soil with formation of potassium salts, which are absorbed by the plant.

Haricot beans were watered with solutions of sodium chloride of gradually increasing concentration until the plant died. The ash contained 11·3 per cent. of chlorine, whereas the ash of similar beans grown in the same soil without addition of sodium chloride contained only 0·53—0·49 per cent. of chlorine. Notwithstanding the large excess of chlorine, the ash contained no sodium, from which it appears that the plant was killed by abnormal absorption of potassium chloride.

Since sodium nitrate is cheaper, and contains a higher proportion of nitrogen than the potassium salt, the latter can only be used with advantage in the case of soils which are poor in potassium compounds.

C. H. B.

**Manuring Experiments in Posen in 1882.** By E. WILDT (*Bied. Centr.*, 1883, 516—520).—Experiments made in 1881 with a liberal application of phosphoric acid and nitrogen gave negative results only, probably owing to a lack of potash in the soil. The present experiments were generally a repetition of the previous ones, with the addition of potash. The experiments were made on five different estates. The nitrogen was added as ammonium sulphate, potash as potassium chloride, the soluble phosphoric acid as Curaçao superphosphate, the phosphoric acid soluble in citric acid as precipitated calcium phosphate, and reverted phosphoric acid as phosphorite superphosphate, half of whose acid was soluble in water, and the other half reverted.

I. Soil, slightly loamy sand 10 inches deep; subsoil lighter, and below siliceous sand. Crop, potatoes; previous crop, rye, with stall manure. Nitrogen was given in every case, along with soluble phosphoric acid

alone in one case, with potash alone in the second case, and with potash and the various phosphates in all other cases. In all plots in this group, the yield was considerably increased, but an economical result was obtained only when potash and soluble phosphoric acid were added together; the phosphoric acid must be present in sufficient quantity, or the increased yield will be that solely due to the potash. The amount of starch in the potatoes was considerably reduced by the chlorine in the potassium salt. The phosphoric acid soluble in citric acid gave only a small increase; but it may be expected to influence the following crop, as another experiment shows: thus, parcels manured the previous year were cropped again without manure. Nitrogen alone gave no increase, whilst all the phosphate manures gave increased yields, and those most backward the first year did best in the second year.

II. Soil, sandy loam, 4 inches deep; subsoil, loam; previous crop, wheat, manured with superphosphate; experimental crop, potatoes. The nitrogen added showed no effect on the crop, on the contrary, the phosphoric acid, and still more the potash, afforded good results; but 10 kilos. per morgen of soluble phosphoric acid gave no better result than 5 kilos.; the action of the reverted acid is not perceptible, and the result of the acid soluble in citric acid is said to be inexplicable, because the yield is the same as with soluble acid.

III. Soil, sandy loam, 1 foot deep; subsoil, loamy marl. From 1874 to 1880 lucerne was grown; after that summer wheat without manure. The experimental crop was barley. All the manures gave only a slight increase, and in no case do they appear to be economically useful. No conclusion can be drawn as to the action of the various forms of phosphoric acid, the increased yield is so small.

IV. Sandy soil; subsoil sandy, below clay marl. Barley was sown. The potash gave no results; the phosphoric acid acted slightly, and only the nitrogen produced any marked effect, and this was only economically successful when the increased yield of straw was considered.

V. Soil, clayey sand, 8 inches thick; subsoil mixed with marl. Before the experiment no artificial manure had ever been applied, but only a little stable manure. The previous crop was wheat; the experimental crop was oats. Whilst potash and phosphoric acid did not increase the yield, the action of the nitrogen was somewhat considerable, indeed taking into account the straw, a not inconsiderable profit was obtained.

J. T.

**Manuring Experiments on Tobacco.** By J. NESSLER (*Landw. Versuchs.-Stat.*, 29, 309—312).—The chief object of this investigation was to study the effect on the combustibility of tobacco produced by various kinds of manure, such as chloride, sulphate and nitrate of potassium, superphosphate, stable dung, &c. To this end the dried leaves were ignited, and the time during which they continued to glow noted down. Potassium nitrate and sulphate were found to increase the burning properties of the tobacco, whilst potassium chloride produced the opposite effect. The experimental results, however, exhibit great inequalities, partly due, no doubt, to the fact

that the soils were in various states of cultivation in the previous year. Phosphoric acid, however, seems to be not at all an essential constituent of the manure. It is recommended to grow a crop of swedes or beetroot on the land, using a potash manure, and then to follow with tobacco, when Chili saltpetre might be employed.

J. K. C.

**Manuring of Marshy Land.** By H. J. CARSTEN (*Bied. Centr.*, 1883, 564). — Limed and unlimed portions, manured with raw Peruvian guano, gave similar yields, showing that lime was practically without effect. Another portion of new land, treated five years successively with guano, and sown with oats, gave a yield increasing from 36 hl per ha in the first year to 55 hl per ha in the fifth year. From this it would appear that such land can be converted into profitable arable land by the addition of artificial manure alone, without stable or town manure.

J. T.

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## Analytical Chemistry.

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**Use of Ammonium Thiosulphate instead of Sulphuretted Hydrogen in Qualitative Analysis.** By A. ORLOWSKI (*Zeits. Anal. Chem.*, **22**, 357—366).—Barium, strontium, and lead are precipitated as sulphates by adding ammonium thiosulphate to their neutral or slightly acid solutions. The filtrate is acidulated with hydrochloric acid, heated to boiling, and thiosulphate added until no further precipitation of sulphur takes place. The precipitate may contain the sulphides of arsenic, antimony, tin, platinum, gold, silver, copper, mercury, bismuth, and cadmium. These metals are separated from each other in the ordinary way. To the filtrate ammonium chloride, ammonia, and ammonium sulphide are added, precipitating the metals of Group III, besides the sulphide of cadmium, which may not have been completely separated with the previous group. The cadmium is separated from zinc and manganese by adding sodium thiosulphate in excess to the neutral or feebly acid solution, and then boiling. A yellowish-brown precipitate is formed, to which, when cool, hydrochloric acid is added until the evolution of chlorine ceases. The precipitate now consists of hydrated manganese peroxide only; it is collected, and caustic soda in excess is added to the filtrate, the cadmium is thereby precipitated, whilst the zinc remains in solution.

P. F. F.

**An Indicator showing the Neutral Point in Alkalimetry and Acidimetry.** By A. GAWALOWSKI (*Zeits. Anal. Chem.*, **22**, 397).—By mixing alcoholic solutions of phenolphthalein and dimethylaniline-orange (methyl-orange) an indicator is obtained, which turns deep-red in an alkaline and rose-red in an acid solution, whilst in a neutral solution it is pale lemon-yellow.

P. F. F.

**A new Fractioning Apparatus.** By C. WINSSINGER (*Ber.*, **16**, 2640—2645).—This apparatus, which combines both the cooling and washing methods, yields extremely good results. It cannot be succinctly and clearly described without the diagram.

A. K. M.

**A new Form of Hot Filtering Funnel and an Apparatus for Obtaining Sublimates.** By R. RICHTER (*J. pr. Chem.* [2], **28**, 309—310).—By coiling a thin lead tube round an ordinary funnel, and passing steam through it, the filtration of substances, even sparingly soluble in hot alcohol, is readily accomplished. By placing a coil of lead piping, through which cold water is passed, on the upper watch-glass of a pair used for sublimation, the author found it possible to obtain with great ease crystalline needles of substances melting at 26°.

A. B.

**Determination of the Quantities of Gases Dissolved in Watery Liquids.** By A. LONGI (*Gazzetta*, **13**, 479—481).—The author makes use of the apparatus described in his paper "On the Estimation of Nitrous and Nitric Acids" (p. 366 of this volume).

H. W.

**A new Method of Determining Nitrogen in Organic Substances.** By J. KJELDAHL (*Zeits. Anal. Chem.*, **22**, 366—382).—The dried substance is digested in a flask for several hours with a large excess of concentrated sulphuric acid, at a temperature approaching the boiling point of the acid. Some fuming sulphuric acid or a little phosphoric anhydride may, with advantage, be added to combine with any trace of water that may be present. In this manner the greater part of the organic nitrogen is converted into ammonia, and this conversion is completed by oxidation with potassium permanganate, which is added cautiously as a fine powder in very small quantities at a time. The addition of permanganate is continued until the solution becomes green, showing that an excess has been employed. When cold, the liquid is diluted with water, rendered alkaline with a strong solution of caustic soda, and then distilled into a receiver containing a measured quantity of standard acid. The author has obtained satisfactory results with nitrogenous organic substances of the most varied character.

P. F. F.

**Estimation of Nitrogen in Nitro-, Azo-, and Diazo-compounds.** By A. GOLDBERG (*Ber.*, **16**, 2546—2556).—Several unsuccessful attempts have been made by chemists to estimate the nitrogen in nitrates by Will and Varrentrapp's method, by adding a reducing agent to the soda-lime. In the author's experiments stannous sulphide was employed; a mixture of this with soda-lime yielding hydrogen when heated. The results obtained are too low; the addition of sulphur produces somewhat better results, but even then the percentage of nitrogen is generally 1—1.5 too low. This mixture (100 parts soda-lime, 100 parts stannous sulphide, and 20 parts sulphur) yields however satisfactory results with nitro- and azo-compounds. To charge the tube, a layer (5 cm.) of coarsely-powdered soda-lime is



first introduced, then a layer (15—20 cm.) of the mixture through which the substance is distributed in the usual way by means of a wire, then another layer (5—10 cm.) of the mixture alone, and finally coarsely powdered soda-lime. The ammonia is absorbed by means of dilute sulphuric acid, and titrated with baryta-water. In the case of the azo-compounds the method is more troublesome than in that of nitro-compounds, owing to the chemical indifference of the former class of substances and to the readiness with which they sublime; the difficulty is overcome, however, by employing a longer tube. When moderately stable, diazo-compounds, such as diazosalicylic acid and paradiazobenzenesulphonic acid, are treated as above, they yield either no ammonia, or at most a very small percentage.

A. K. M.

**Detection of Nitric Acid in presence of other Acids capable of Interfering with its Reactions.** By A. LONGI (*Gazzetta*, **13**, 468—469).—In testing for nitric acid in solutions containing ammoniacal salts, together with chlorates, bromates, iodates, chromates, and other oxidising salts, an error may arise from the conversion of part of the ammonia into nitric acid by the oxidising action of those salts, whence it may appear that nitric acid was present in a solution which previously contained none. This source of error may, however, be avoided by treating the solution with sulphurous acid before heating it, the bromates, chlorates, &c., being thereby reduced to bromides, chlorides, &c., while the nitric acid remains either as such, or in the form of a sulphuroso-nitric compound in which the nitric acid may be detected by the ordinary tests. Bromine and iodine, if present, may be eliminated by G. Vortmann's method (*Ber.*, **13**, 2024). Lead dioxide does not oxidise ammoniacal salts in a solution containing acetic acid.

H. W.

**Paratoluidine Sulphate as a Test for Nitric Acid.** By A. LONGI (*Gazzetta*, **13**, 465—468).—If to a liquid containing nitrates a few drops of *p*-toluidine sulphate be added, and then a quantity of ordinary sulphuric acid equal in volume to the nitrate solution, and in such a manner that the liquids shall form two distinct layers, a deep red coloration will appear at the surface of separation, changing after some time to a dark yellow. In solutions of chlorates, bromates, iodates, chromates, and permanganates, the same reagent produces a blue coloration of such intensity as completely to mask the red colour produced with nitrates, even when the quantity of either of the salts just mentioned is very small in comparison with that of the nitrate. Aniline sulphate does not produce any coloration with nitrates, but a mixture of the sulphates of aniline and *p*-toluidine (crude aniline oil) produces a deeper red colour than the toluidine alone.

This test for nitrates is less delicate than that which is afforded by brucine or by diphenylamine, the former of which produces a red colour in solutions containing only 1 part of nitric acid in 256,000 parts of liquid, the latter a blue colour, sensitive to 1 part in two millions; but the toluidine test has the advantage of not giving the same colour with chlorates, bromates, &c., or with nitrites, with which it develops a yellow coloration gradually passing into red.

H. W.

**Volumetric Estimation of Nitric Acid.** By A. LONGI (*Gazzetta*, 13, 482—485).—The blue colour produced by diphenylamine in a solution of nitric acid is destroyed by stannous salts, and this reaction may be made available for the volumetric estimation of nitric acid. The salt employed is Marignac's stannoso-stannic sulphate, and its reaction with nitric acid may be represented by the equation  $4\text{SnSO}_4 + 4\text{H}_2\text{SO}_4 + 2\text{HNO}_3 = 4\text{Sn}(\text{SO}_4)_2 + 5\text{H}_2\text{O} + \text{N}_2\text{O}$ , showing that 4 mols. of the stannous salt are required for the decomposition of 2 mols. nitric acid, or 2 mols.  $\text{SnSO}_4$  for 1 mol.  $\text{HNO}_3$ .\* The method is especially applicable to the estimation of small quantities of nitric acid.  
H. W.

**Estimation of Nitrous and Nitric Acids, separately or together.** By A. LONGI (*Gazzetta*, 13, 469—479).—For the estimation of nitrous acid, the author makes use of the well-known reaction with urea and acetic acid. Nitrates are first reduced to nitrites with hydrochloric acid and arsenious acid. The paper contains a description of the apparatus employed, and tables of analytical results.  
H. W.

**Estimation of Iodine in presence of Chlorine and Bromine by means of Ferric Sulphate.** By A. GAVAZZI (*Gazzetta*, 13, 327; and 454—455).—Duflos' process for determining the amount of iodine in iodides by boiling them with ferric chloride and condensing the vapours in a concentrated solution of potassium iodide is not applicable when bromides are present, as bromine passes over along with the iodine. If, however, ferric sulphate be substituted for the chloride, this difficulty is obviated, the iodine alone being volatilised; but the sulphate should be heated to a little below redness to remove free acid, and it is as well to add a little ferrous sulphate to increase the solubility of the ferric salt. This reaction can be employed in testing commercial potassium iodide for chlorine, as all the chlorine remains in the retort quite free from iodine. The method is also useful for detecting traces of iodine in mixtures containing large quantities of chlorine and bromine; and may be used, moreover, for preparing pure iodine.  
C. E. G.

**Assay of Commercial Potassium Iodide.** By W. LENZ (*Zeits. Anal. Chem.*, 22, 391—393).—The author has investigated the method of assaying potassium iodide by means of a standard solution of mercuric chloride. He finds that the results are inaccurate, the end-point of the reaction being greatly influenced by temperature.  
P. F. F.

**A new Microchemical Test for Sodium.** By A. STRENG (*Jahrb. f. Min.*, 1883, 2, Ref., 365).—The author proposes to employ uranium acetate as a test for sodium; by its action on any sodium solution, crystals of uranium sodium acetate are formed, which are but sparingly soluble in water. They appear in the form of tetra-

\* In the original paper it is said that 4 mols. of the stannous salt are required to decompose 1 mol. nitric acid; but this is clearly inconsistent with the equation above given.

hedra, and these minute yellow crystals cannot be mistaken for the rhombic crystals of uranium acetate, which separate out as the solution dries, on account of their action on polarised light. The reaction is very sharp, as the double salt contains a very low percentage of soda (6.6 per cent.).

B. H. B.

**Detection and Estimation of Zinc and Lead in Presence of Iron.** By A. DEROS (*Compt. rend.*, **97**, 1068—1070).—*Zinc*.—The hydrochloric acid solution of 1 gram of the substance is poured gradually, with agitation, into an excess of ammonia, and when cold the mixture is electrolysed in a platinum capsule which acts as the positive electrode, the negative electrode consisting of a platinum spatula or a coil of platinum wire. The current employed should give 300—400 c.c. of defonating gas per hour. Care must be taken to keep the liquid ammoniacal, and after three or four hours the negative electrode is withdrawn, carefully washed, and then treated with a few drops of dilute sulphuric acid, which dissolves the greyish deposit. The solution is evaporated to dryness in a platinum dish with addition of a few drops of cobalt solution and strongly heated; a green residue shows the presence of zinc.

In order to estimate the zinc, the solution of 1 gram of the substance is treated as just described, the negative electrode consisting of a sheet of platinum 3 cm. broad and 4—5 cm. long. After 12 hours the zinc will be completely precipitated, which can be proved by placing a new electrode in the liquid. The negative electrode is rapidly washed by immersing it in water, care being taken not to detach any of the somewhat loosely adhering deposit, and is then immersed in a solution of potash or soda of 8° or 10° B., which dissolves only the zinc. The alkaline solution is again electrolysed, the zinc being deposited as a firmly adherent crust on a weighed platinum cone. The deposit is washed successively with water, alcohol, and ether, and dried at 90—100°. It is advisable to wash with water before interrupting the current.

*Lead*.—1 gram of the finely powdered substance is placed in a conical flask with 3 or 4 grams of pure cadmium, and very gently warmed with dilute hydrochloric acid. When the solution is complete, and no bubbles of gas are given off from the cadmium, the lead is completely precipitated. The liquor is carefully decanted off, and the residue washed several times by decantation. 5 or 6 c.c. of nitric acid are then added, and the solution of lead and cadmium is transferred to a crucible which acts as the negative electrode, the positive electrode being a weighed platinum cone. Rather less battery power is required than in the case of zinc, and in four or five hours the lead is completely precipitated on the positive electrode in the form of peroxide, which is washed with water, dried, and weighed. This process will detect 0.0005 gram of lead in 1 gram of substance.

C. H. B.

**Volumetric Estimation of Iron by means of Sodium Thio-sulphate and Salicylate.** By G. BRUEL (*Compt. rend.*, **97**, 954—955).—It is well known that when solutions of ferric salts are mixed with sodium salicylate a deep violet colour is produced. If sodium

thiosulphate is now added to the slightly acidified solution, the iron is converted into a double ferrous sodium thiosulphate, and the colour is discharged. To estimate iron by means of this reaction, dissolve 1 gram of pure iron in 20 c.c. of hydrochloric acid, with addition of potassium chlorate, boil until all chlorine is expelled, and then dilute to 1 litre. Prepare also a solution of sodium thiosulphate containing 1 gram per litre. Take 10 c.c. of the ferric solution, dilute with four times the volume of water, heat to boiling, and add 0.1 gram of sodium salicylate. Then add the thiosulphate solution drop by drop from a burette, until the liquid has only an almost inappreciable rose tint. Having thus standardised the thiosulphate, the total amount of iron in a salt or mineral, or the relative proportions of ferrous and ferric iron in any substance, may be determined in a similar manner. In the latter case the ferric iron is determined in 1 part of the solution after acidifying with hydrochloric acid, and the total iron is estimated after boiling with potassium chlorate and hydrochloric acid.

C. H. B.

**Detection of Manganese in Presence of Zinc, and of Bismuth in Presence of Lead, by Electrolysis.** By A. GUYARD (*Compt. rend.*, **97**, 673—674).—Calamine, zinc slag, &c., is treated with dilute sulphuric acid, the solution allowed to clarify by standing, and then electrolysed, the negative electrode being of copper or brass, and the positive electrode of platinum. In a short time the liquid round the positive electrode is coloured violet by permanganic acid. In testing metallic zinc, the latter is fused in contact with air, and the scum of oxides which forms is treated as above.

When a concentrated solution of pure zinc sulphate is electrolysed, the negative electrode being platinum, and the positive electrode a sheet of commercial lead, the lead becomes gradually covered with a layer of lead dioxide, and any bismuth or copper present in the lead is deposited with the zinc on the negative electrode. On treating the latter with dilute sulphuric acid, the zinc is dissolved and the copper and bismuth are left undissolved, and may be separated by the usual methods.

C. H. B.

**Detection of Arsenic.** By E. REICHARDT (*Arch. Pharm.* [3], **21**, 271—279).—After noticing the occurrence of arsenic in different pigments, &c., and the legal prohibition of the use of arsenical compounds for colouring papers, foods, &c., the author describes Fleck's modification of Marsh's test, which has been recommended for the detection of small quantities of arsenic. While admitting the improvement in this modification, the author does not recommend Marsh's test for general use, but prefers, as simpler and safer, to pass the arsenic hydride through a solution of silver nitrate, which has been rendered strongly acid with pure nitric acid. In this way the tenth of a milligram of arsenious oxide can be detected. Marsh's test, in which an arsenic mirror is obtained, cannot be quantitatively applied, but this process can be at once qualitatively and quantitatively used. After precipitation has ceased, bromine is added to the silver solution, and the arsenic precipitated as magnesium ammonium arsenate.

For further particulars concerning this method see Abstr., 1881, 195. W. R. D.

**Determination of Organic Matter in Water.** By A. R. LEEDS (*Phil. Mag.* [5], 169, 13).—In this paper is described a process for the determination of organic matter in potable water, based upon the readiness with which metallic silver is separated from solutions of its salts by organic matter. The details of the process are as follow:—To 250 c.c. of the water to be examined, 100 c.c. of decinormal silver nitrate solution are added, and the mixture allowed to stand for about two days, when the solution will have become clear, the entire precipitate collecting at the bottom. This precipitate is washed first with ammonia, to get rid of the chloride, and then dissolved in nitric acid, the amount of silver being subsequently determined by Pisani's process. On comparison of this with the permanganate process, it was found that sometimes the former, sometimes the latter, gave the higher result; the general inference was deduced from the results that, whilst a solution of potassium permanganate was reduced to a greater or less extent by most organic substances soluble in water, the silver nitrate is the more readily reduced by easily decomposing organic compounds, akin in their nature to sewage. V. H. V.

**Prothistological Examination of Potable Waters.** By L. MAGGI (*Gazzetta*, 13, 323).—Cartes has proposed the use of a solution of osmic acid (1.5 : 100) to detect the presence of so-called microbes in potable waters: 1 part of the solution added to 30 or 40 of water kills the organisms, which then settle to the bottom of the vessel, and can be detected by microscopic examination of the deposit. The author, on the supposition that they were killed and rendered invisible from induration produced by the action of the osmic acid, tried other reagents, and obtained satisfactory results with a solution of palladium chloride (1 : 800), and also with hæmatoxylin, methyl-violet, magenta, and Lyons blue. C. E. G.

**Petroleum Testing.** By F. BEILSTEIN (*Zeits. Anal. Chem.*, 22, 309—316).—The author has examined the methods of determining the flashing point devised by Abel, Engler, and others. These methods yield concordant results only when the apparatus used is of precisely the same dimensions. The method least open to this objection is that devised by L. Liebermann (Abstr., 1882, 1326) and developed by Stoddard (Abstr., 1883, 517). The author finds that with Stoddard's apparatus the results are concordant, even when the dimensions are different, provided the length of the tube is five, six, or seven times its breadth. The author, by employing a slightly modified form of Stoddard's apparatus, obtained results agreeing within 0.25°, thus securing greater accuracy than with any previously known method of testing. The author further points out the greater importance of testing petroleum by distillation, which not only determines whether the oil is safe or not, but also shows its fitness or unfitness for lighting purposes. By distillation, petroleum may be broken

up into three fractions: light oil, boiling under  $150^{\circ}$ ; burning oil (kerosene), boiling at  $150-270^{\circ}$ ; heavy oil, boiling above  $270^{\circ}$ . The author considers that good mineral oil for lamps should contain less than 5 per cent. of light, and not more than 15 per cent. of heavy oil. A higher percentage of heavy oil in American is much more objectionable than in Russian petroleum, as in the latter the heavy oil is more readily raised by the wick. Thus, a Russian petroleum, with 20 per cent. of heavy oil, was found to be well adapted for lamps. If lamps were constructed with the summit of the wick nearer the surface of the oil, it would be possible to consume petroleum with considerably higher proportions of heavy oil; the price would thereby be reduced, the safety increased, and as the author asserts, the American oil displaced from the European market by the Russian.

P. F. F.

**Action of Iodine Pentabromide on Essential Oils.** By M. FORNEY (*Arch. Pharm.* [3], **21**, 311).—The action of iodine pentabromide on the principal essential oils was examined in reference to the colour which is produced with the pure oils alone; also when mixed with 25 per cent. of turpentine oil, and when dissolved in 25 per cent. of alcohol (95 per cent.). The results are recorded in a table.

W. R. D.

**Alcohol in the Brain in Cases of Inebriation.** By H. F. KUIJPER (*Zeits. Anal. Chem.*, **22**, 347–357).—The author describes the detection of alcohol in the stomach, brain, and liver of two persons supposed to have died in a state of inebriation.

P. F. F.

**Detection of Bordeaux Red in Wine.** By C. THOMAS (*Arch. Pharm.* [3], **21**, 304–305).—The colouring matter is absorbed from the wine by silk, which is washed with cold water, and then heated with boiling water, when the artificial colouring matter is dissolved, but the natural colouring matter remains on the silk. In the red liquid so obtained, sulphuric acid develops a violet colour, and ammonia a chestnut-brown. In the estimation of the potassium sulphate by precipitation as barium sulphate, the Bordeaux red is carried down with the precipitate to which it remains attached. When this precipitate is ignited, an aromatic odour resembling naphthalene and nitrobenzene is noticed.

W. R. D.

**Estimation of Glucose.** By P. LAGRANGE (*Compt. rend.*, **97**, 857–858).—The precipitate formed on adding lead acetate to a solution of sugar, carries down with it a considerable proportion of the glucose. An accurate determination of this substance cannot therefore be made in the filtrate from the lead acetate precipitate, but must be made in the original liquid.

C. H. B.

**Starch Varieties detected by the Swelling Process.** By W. H. SYMONS (*Bied. Centr.*, 1883, 571).—The author proposes to use instead of definite temperatures, alkaline solutions of definite strength. The most suitable are caustic soda solutions of 0.5–1.5 per cent. strength; 1 gram of the starch is repeatedly stirred up with 1 c.c. of the particular soda solution, and after ten minutes examined under

the microscope. It is then found that with one solution very few granules are swollen; with a stronger solution, the greater part are swollen; and with a more concentrated still, all are swollen. The following table gives the results for various starches:—

	Order of magnitude of the granules.	Few granules swollen with	Greater number of granules swollen with	All granules swollen with
		P.c. NaHO.	P.c. NaHO.	P.c. NaHO.
Potato.....	2	0·6	0·7	0·8
Oat .....	8	0·6	0·8	1·0
Natal.....	4	0·7	0·8	1·0
Tous-le-Mois .....	1	0·7	0·9	1·0
Wheat.....	5	0·7	0·9	1·0
Bermuda.....	4	0·8	0·9	1·1
Sago .....	3	0·8	0·9	1·1
Maize .....	6	0·8	1·0	1·1
Cassava .....	7	0·8	1·0	1·1
St. Vincent.....	4	0·9	1·0	1·2
Rice.....	9	1·0	1·0	1·3

J. T.

**Detection of Hydrocyanic Acid.** By C. BRAME (*Arch. Pharm.* [3], 21, 307).—The author has noticed that hydrocyanic acid precipitates albumin from solution, and this occurs when the vapour of hydrocyanic acid is passed into a solution of albumin. For the detection of the acid in toxicology where owing to decomposition it cannot be directly recognised, the author proposes to detect the ammonium formate in the liquid after evaporation over sulphuric acid in a vacuum.

W. R. D.

**Pyroligneous Acid.** By G. VULPIUS (*Arch. Pharm.* [3], 21, 256—260).—The author proposes to test the strength of the rectified pyroligneous acid, which is official in the German Pharmacopœia, not only with regard to the amount of acetic acid which it contains, but also in reference to the empyreumatic bodies present. The first is accomplished in the ordinary way with a standard solution of sodium hydroxide, using phenol-phthaleïn as indicator. The author estimates the empyreumatic constituent with a standard solution of potassium permanganate; 10 grams of the acid are diluted to 400 c.c. with water, acidulated with hydrochloric acid, and titrated until the colour of the potassium permanganate is permanent after one minute. A rectified pyroligneous acid should not contain less than 6 per cent. of acetic acid, and should decolorise at least ten times its volume of the standard solution of potassium permanganate recognised by the German Pharmacopœia. It should also become sensibly darker in colour when exposed to sunlight.

W. R. D.

**Trustworthiness of Berthelot and Fleurieur's Method for the Estimation of Tartaric Acid.** By P. FERRARI (*Landw.*

*Versuchs.-Stat.*, **29**, 353—354).—According to Amthor, this method does not answer for plastered wines, as these contain acid potassium sulphate, which on addition of alcohol and ether, is in part thrown down and then titrated as cream of tartar. The author, however, proceeds to show that this is not the case; when a solution of acid potassium sulphate is treated with a mixture of alcohol and ether, neutral potassium sulphate is thrown down, and sulphuric acid is left in solution, a result which does not vitiate the figures obtained by the above method.

J. K. C.

**Potassium Tartrate in Plastered Wine and Estimation of Tartaric Acid.** By P. PICARD (*Bied. Centr.*, 1883, 559).—The diminution in the amount of potassium tartrate contained in wine which has been treated with gypsum in the cask, is ascribed by the author to the fact that the former salt is not in a position to saturate a solution containing a certain amount of potassium sulphate. The precipitation of potassium bitartrate by potassium sulphate is employed by the author to quickly estimate the former salt in wines. Free tartaric acid hinders the estimation through forming bisulphate with simultaneous separation of bitartrate. The method is also not applicable to plastered wine, which always contains free tartaric acid, but good results are obtained with unplastered common wines, which but rarely contain any free tartaric acid. Malic, benzoic, and other acids usually found in wines do not influence the result.

J. T.

**Detection of Salicylic Acid in Dietetic Substances.** (*Arch. Pharm.* [3], **21**, 296).—Salicylic acid may be detected in liquids by diluting with water and distilling; the distillate is then tested with ferric chloride. When only a small quantity of salicylic acid is present, the first fraction of the distillate contains no salicylic acid, subsequent fractions easily give the reaction. In this way, 0.005 per cent. of the acid can readily be detected. Salicylic acid does not distil with the water if alcohol or tannic acid is present; in the latter case the liquid should be acidulated with dilute sulphuric acid before distillation. Salicylic acid in butter is detected by distilling with water and testing as above. When the volume of the distillate is large, it is made alkaline with ammonia evaporated to dryness, and the residue tested with ferric chloride. The ferric chloride reaction is not obtained in presence of free acids, alkalis, or large quantities of salts.

W. R. D.

**Volumetric Method for the Estimation of Fat in Milk.** By L. LIEBERMANN (*Zeits. Anal. Chem.*, **22**, 383—390).—50 c.c. of the milk are placed in a glass cylinder and treated with 5 c.c. of a solution of potassium hydroxide (sp. gr. 1.2); 50 c.c. of washed ether are then added and the contents of the cylinder well shaken for two minutes. The liquid is allowed to separate, and then 20 c.c. of the ethereal layer are taken out with a pipette and placed in a small flask (about 50 c.c.), the capacity of which is accurately known. The ether is evaporated on a water-bath, and the flask is then heated for 15 minutes to 100—105°, care being taken to avoid any bubbles forming in the melted butter. The flask is plunged into water at the atmo-



spheric temperature, causing the butter to solidify on the bottom of the flask, which is now nearly filled with a measured quantity of water from a burette, and then exactly filled by delivering the water from a small graduated pipette. The difference between the volume of water required and the capacity of the flask indicates the volume of butter in 20 c.c. of the milk. On multiplying by 5, the percentage of fat by volume is obtained, and by means of a table the corresponding percentage by weight can be ascertained. The results agree very closely with those obtained by the ordinary gravimetric methods. P. F. F.

**Separation of Morphine in Toxicology.** By E. SCHEIBE (*Arch. Pharm.* [3], 21, 290).—The author recommends the following process for the separation of morphine from organic matter. The solid residue is extracted repeatedly with acidulated water, filtered, evaporated to a syrup at 100°, and then extracted with four or five times its volume of alcohol (90 per cent.), and again filtered. The alcoholic liquid is distilled, the residue in the retort filtered, and the filtrate successively extracted with amyl alcohol until colouring matter ceases to be removed. The acid liquid is warmed to 50° or 60°, mixed with an equal volume of amyl alcohol, rendered alkaline with ammonia, and agitated; the amyl alcohol is separated, and the alkaline liquid again extracted with amyl alcohol. The two quantities of amyl alcohol are mixed, then distilled, and the residue extracted by acidulated water with the aid of a gentle heat. After filtering, the acid filtrate, which should be again extracted with amyl alcohol, is mixed with 10 parts of anhydrous ether and 1 part of alcohol, and made alkaline with ammonia. After agitation, the ether-alcohol is run off, and the liquid several times extracted with more of the mixture. The morphine is obtained free from colouring matter on evaporating the ether-alcohol solution. W. R. D.

**Determination of Ammonia in Vegetable Juices and Extracts.** By E. BOSSHARD (*Zeits. Anal. Chem.*, 22, 329—347).—The results obtained, both by Schlösing's method of treatment with lime-water in the cold and that of distillation with magnesia, are too high if asparagine or glutamine are present, the latter being by far the more objectionable of the two. Tolerably accurate but somewhat low results may be obtained, however, if these amides are first precipitated with mercuric nitrate, and the filtrate, after removal of the excess of mercury by sulphuretted hydrogen, is distilled with magnesia. Satisfactory results are also obtained by acidulating the vegetable extract with hydrochloric or sulphuric acid, and then precipitating the ammonia with phosphotungstic acid. The precipitate is filtered after two hours, washed with more of the phosphotungstic acid solution, then dissolved in hot water, and distilled with magnesia.

P. F. F.

**Detection of Asparagine and Glutamine in Vegetable Juices and Extracts.** By E. SCHULZE (*Zeits. Anal. Chem.*, 22, 325—328).—The author has previously shown that glutamine, an amide of

glutamic acid, is present in beetroot juice and in the sprouts of gourds (this Journal, 1877, i, 104, and ii, 324), and also that this glutamine is a homologue of asparagine (Abstr., 1883, 658). It may not unnaturally be inferred, therefore, that glutamine is as widely distributed in the vegetable kingdom as asparagine. The two amides may be detected by precipitation with mercuric nitrate. The juice or extract is precipitated first with basic lead acetate and then with mercuric nitrate. If either of the amides is present, the mercuric precipitate when decomposed with sulphuretted hydrogen yields a solution which evolves ammonia when heated with caustic alkalis, and dissolves cupric hydrate to a deep blue solution. Allantoin would also be precipitated with mercuric nitrate, but would not give the reaction with cupric hydrate, and it is also easily distinguished by being precipitated with silver nitrate and ammonia. In order to prove the presence of asparagine and glutamine in the solution obtained as above, it is necessary to isolate them or their products of decomposition, aspartic and glutamic acids. By neutralising the solution with ammonia and evaporating to a small bulk, the asparagine is readily obtained in the crystalline form, and afterwards by boiling the solution with hydrochloric acid, the glutamine is converted into glutamic acid, of which the lead salt may be prepared by adding basic lead acetate, filtering, and after concentrating the filtrate, precipitating the lead salt by alcohol. P. F. F.

**Analysis of Flour.** By BALLAND (*Compt. rend.*, 97, 496—497).—The quantity of gluten obtained from the same flour varies with the mode of operation, and especially with the degree of hydration of the gluten and the amount of washing. The proportion of water of hydration is higher in gluten from soft wheat than in that from hard wheat, and in gluten from fresh paste than in that from paste which has stood for two hours; it is also higher in gluten from old flour. Sodium chloride, ammonium acetate, potassium carbonate, glycerol, and certain other substances, have the power of dehydrating gluten, which loses weight and becomes hard: in contact with a large quantity of water, however, the gluten reabsorbs water, and regains its original weight and properties. On prolonged washing, gluten loses weight, the loss being greater with gluten from soft wheat than with that from hard wheat, with gluten from paste, which has stood two hours than with that from fresh paste, and with gluten from old flour than with that from new flour. Gluten from new flour, if placed in water for 24 hours and then washed, loses about 10 per cent., whilst gluten from old flour loses more than 20 per cent. under the same conditions.

In order to estimate gluten, 50 grams of flour are made into a paste with 20 to 25 grams of water, and allowed to stand 25 minutes. The paste is then divided into two equal portions, from one of which the gluten is extracted immediately, whilst the other is allowed to stand an hour. As soon as the wash-water is clear, the gluten is tightly squeezed and weighed. It is then washed for five minutes more, and again weighed. Four numbers are thus obtained, and the mean of these is taken as the amount of gluten present. C. H. B.

**Chloroform-water and Ether in Dialysis.** By H. STRUVE (*Bied. Centr.*, 1883, 569).—The author remarks on the defects of parchment-paper, and recommends bladder. Substances containing animal or vegetable albumin are apt to decompose during the long time usually required for dialysis. To prevent this decomposition, the author proposes chloroform-water for the outer liquid, which, on account of its powerful antiseptic properties, hinders decomposition. In long operations, it is also advisable to place some chloroform-water directly with the substance under treatment. The author also recommends ether as the outer fluid with bladder as diaphragm. Fresh bruised malt so treated gave sugar and diastase. Beer-yeast similarly treated gave a solution with strong inverted rotative power, due to sugar; it contained also leucine, tyrosine, phosphoglyceric acid, albumin, and peptone. The residue within the bladder consisted of a thick pap, containing white round bodies which on analysis proved to be pure tyrosine. The yeast dried at 100° had the following composition:—

Albumin.....	1·29
Invertin .....	4·19
Extractive matter.....	51·12
Yeast residue.....	42·02
Ether residue.....	1·38

The ether residue remained as crystalline needles, which were not cholesterin. J. T.

**Estimation of Chloroform in the Blood of an Anæsthetised Animal.** By GRÉHANT and QUINQUAUD (*Compt. rend.*, 97, 753—755).—96 c.c. of blood are taken from an artery or vein out of contact with the air, and are distilled in a vacuum. Gases are given off at 45°, and liquid passes over at 63°. Almost all the chloroform is given off with the gases, and is removed from the latter by agitating four or five times with successive quantities of water out of contact with the air. The wash water and the distillate are mixed, and the volume carefully noted; 18·7 c.c. of the mixed liquid is heated in a sealed tube at 100° with 1 c.c. of Barreswil's cupro-potassium solution, the air having been expelled by a current of carbonic anhydride. A similar blank experiment is made with the cupro-potassium solution and distilled water, since the latter sometimes exerts a reducing action. If the 1 c.c. of cupro-potassium solution is not completely reduced, a second experiment is made with 18·7 c.c. of the liquid and less than 1 c.c. of the copper solution, and if necessary the experiment is repeated until the amount of the cupro-potassium solution, which is just reduced by the 18·7 c.c. of the liquid to be examined, is ascertained.

The cupro-potassium solution is standardised by means of a solution of 0·5 c.c. of chloroform in 2800 c.c. of distilled water.

A number of experiments show that the blood of an anæsthetised animal contains 1 gram of chloroform in 1800—2181 c.c. of blood, or about 1 gram of chloroform in 2000 c.c. of blood. Other experiments prove that the amount of chloroform necessary to produce insensibility is only very slightly smaller than that which causes death.

C. H. B.

**Detection of Blood Stains on Washed Clothes.** By C. HUSSON (*Compt. rend.*, **97**, 955—956).—When the microscope and spectroscope have failed to detect hæmoglobin or hæmatin, it is not advisable to rely on the detection of fibrin, as this process is liable to many serious errors. It may be useful, however, to ascertain whether special pains have been taken to wash the suspected spots. If this is the case, those parts of the fabric will in all probability retain a small quantity of soap, and the object of the examination is to detect this substance. A small portion of the suspected cloth is heated with water on a watch-glass at 40° for about two hours, care being taken to replace the evaporated water. The cloth is then squeezed, and the liquid evaporated drop by drop on a glass slip, and the residue moistened with a drop of a 1 per cent. solution of potassium iodide or chloride. The same piece of fabric is treated on the watch-glass with a small quantity of acetic acid, and the solution is carefully evaporated on the first residue on the glass slip. A cover-glass is now placed over the residue, and glacial acetic acid is introduced between it and the slip, and then heated to boiling. If hæmatin is present, crystals of the hydrochloride will be seen. If soap is present, yellow oily drops of oleic acid, and characteristic needles of margaric acid will be visible. These needles are frequently more or less contorted, and if the amount of soap is considerable, they aggregate, sometimes forming fibrous bundles, which closely resemble fibrin in appearance. It is mainly for this reason that filaments of fibrin alone, without any hæmatin, cannot be regarded as proof of the presence of blood.

If there is sufficient cloth, another portion is boiled with water, filtered, and the solution evaporated to dryness and ignited in a platinum dish. The residue is moistened with water and tested for alkali with litmus-paper. C. H. B.

**Separation of Wheat Meal from Rye Meal.** By KJÄRSKE (*Arch. Pharm.* [3], **21**, 292).—The meals are first treated with very dilute potash solution and allowed to stand for 24 hours. The liquid is then decanted, the meals shaken with water and allowed to stand for some time. The largest starch granules are formed at the bottom of the vessel, above them a layer of husks and small starch granules, and above these the smallest starch granules. The starch is removed and the husks are submitted to further examination. W. R. D.

**Chemical Properties of the Violet Colouring Matter in Ergot and its Detection in Flour.** By R. PALM (*Zeits. Anal. Chem.*, **22**, 319—323).—The assumption that the violet colouring matter in ergot is combined with alkaline earths is erroneous, because both aqueous and alcoholic ammonia completely extract this colouring matter from ergot, and from such ammoniacal solutions, the colouring matter is wholly reprecipitated by solutions of alkaline earths. The colouring matter is insoluble in absolute alcohol and ether, but soluble in water and in spirit of 20—50 per cent. It gives a slate-blue precipitate with lead acetate, which becomes rose-red on adding concentrated sulphuric acid. Small proportions of ergot may be detected in flour in the following manner:—The thoroughly dried flour is

digested at 30—40° with 10—15 times its weight of alcohol (35—40 per cent. Tralles.), to which a few drops of ammonia have been added. The filtered extract is then completely precipitated with basic lead acetate, collected, and, after being well pressed, digested at a gentle heat with a cold saturated solution of borax. In the presence of ergot, the borax solution assumes a characteristic violet colour; and on adding concentrated sulphuric acid, the colouring matter is precipitated in violet flocks. In this manner, 0·05 per cent. of ergot can be detected in flour. In order to detect ergot in bread, the latter is dried, pulverised, and gently heated for 5—10 minutes with 10—15 times its weight of alcohol (40 per cent.). The solution after being filtered through charcoal is evaporated nearly to dryness on the water-bath, and the residue again extracted with alcohol (40 per cent.). The extract is again filtered through charcoal and then completely precipitated with normal or basic lead acetate. The quantity of precipitate serves as an indication of the proportion of ergot in the bread. Ordinary ergot yields on an average 8 per cent. of such a precipitate. By this process the author could not detect less than 1 per cent. of ergot with certainty.

P. F. F.

**Estimation of Copaiba Balsam.** By H. HAGER (*Arch. Pharm.* [3], 21, 289).—The Maracaibo balsam, which is official in Germany, should yield a clear solution when mixed with  $1\frac{1}{2}$  volumes of alcohol of 90 per cent. Turbidity may indicate the presence of resin oil, colophony, gurgun balsam, or fixed oil. If the solution remains clear, it should be further diluted with about 1 volume of alcohol. This liquid should be very turbid; if it is only slightly so, castor-oil or turpentine-oil is present. Sassafras-oil cannot be detected in this way.

W. R. D.

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## Technical Chemistry.

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**Gases Occluded by Coke.** By F. H. STORER and D. S. LEWIS (*Amer. Chem. J.*, **4**, 409—426).—The only satisfactory method of obtaining the gases occluded by porous substances is by heating in the vacuum produced by means of a Sprengel pump. Reichardt's method (*Jahresb.*, 1866, 53) does not yield good results, and in particular appears to extract the occluded nitrogen with much greater readiness than the carbonic anhydride, the figures for the latter always showing an enormous deficiency in comparison with those obtained by means of the Sprengel pump. It was found, in general, to be impossible to get rid of all the entangled air which clung to the coke, either by immersion in water or by subjection to a current of nitrogen. Numerous analyses are given. The figures quoted below give the results of heating at 200° in a vacuum, after previous treatment with a current of pure nitrogen and exhaustion at the ordinary temperature.

A. Air-dried coke from dwelling house. B. Air-dried coke from store house. C. Old coke from a heap that had been exposed to the weather for three years or more.

	A.	B.	C.
Carbonic anhydride .....	51.46	74.51	60.78
Oxygen.....	4.06	0.42	1.10
Carbon monoxide .....	0.59	1.21	—
Nitrogen (by difference).....	43.89	23.86	—

A. J. G.

**Glacialin.** By BESANA (*Arch. Pharm.* [3], 21, 296).—This substance, which is used as an antiseptic, consists of 18 parts of boric acid, 9 parts of borax, 9 parts of sugar, and 6 parts of glycerol. Another antiseptic called *Glacialin-salt* is entirely boric acid.

W. R. D.

**Extraction of Perfumes and Essential Oils.** By L. NAUDIN (*Pharm. Journ.* [3], 14, 44—48).—This paper contains an account of the various processes which have been proposed for the extraction of perfumes and essential oils from plants, and the disadvantages which accompany their use. The author describes in detail a process which he has successfully applied for the isolation of perfumes in a great state of purity. The plants, &c., are extracted in a vacuum by solvents of very low boiling point, such as butane, pentane, methyl and ethyl chlorides, and light petroleum, without the aid of heat. A diagram of the apparatus employed is given in the paper. The perfumes obtained in this way are not contaminated by any foreign odour, and are not liable to spontaneous alteration, because they are not associated with other constituents of the plants which in decomposing destroy the characteristic odour.

By the use of a mixture of butane and pentane, the author has been able to obtain the distinctive odour from roasted coffee, and also from different kinds of tea, toasted bread, human skin, &c. The time of day at which a flower is collected has an appreciable influence on the perfume which is subsequently obtained: thus, the pink only yields its perfume when collected two or three hours after exposure to sunlight, and false acacia gives a different perfume when gathered in the morning, midday, or evening. The author considers that in many essential oils the hydrocarbon is not the source of the perfume, neither is the fat of many aromatic fatty oils, but that these substances hold in solution a minute quantity of some highly odorous compound which has not yet been isolated.

W. R. D.

**Formic Acid in Rum.** By E. LIST (*Arch. Pharm.* [3], 21, 290).—The author has tested different specimens of rum by neutralising with soda, evaporating to dryness, dissolving the residue in water, and then distilling under diminished pressure, after acidifying with dilute sulphuric acid. The distillate powerfully reduced silver nitrate solution, from which it is inferred that formic acid was present in the rum, having been produced during the fermentation of the cane-sugar molasses.

W. R. D.

**Colour Mordants for Wood.** (*Dingl. polyt. J.*, **249**, 143.)—Godeffroy criticises the erroneous statements found in books concerning wood mordants, and recommends the following process for obtaining a red colour on wood :—A solution of potassium thiocyanate is prepared and the wood immersed therein, after which it is dried and painted with a solution of a ferric salt. Potassium ferrocyanide and cupric sulphate or uranium acetate give brown tints. D. B.

**Novelties in Calico Printing.** (*Dingl. polyt. J.*, **249**, 35—37.)—In the *Bulletin de Rouen*, 1882, 577, Blondel discusses the use of bismuth sulphide in calico printing. Naquet's patents for the application of this substance in dyeing hair are published in the *Moniteur Scientifique* (September, 1882). On account of its high price, bismuth is of but little use in dyeing and printing. Naquet's solution is colourless; the bleached cotton steeped therein and subsequently dried at 25° to 30° gradually develops a light chestnut-brown colour, which, when steamed, changes to chocolate brown. By treating the steamed fabric with a weak solution of sodium thiosulphate, a still darker shade is produced. These colours resist extreme soaping. Naquet uses the following mixture :—100 parts bismuth, 280 nitric acid, 75 tartaric acid, 0·06 ammonia, and 75 sodium thiosulphate.

Balanche prepares a manganese brown in the following manner :—He found that by mixing a solution of potassium dichromate with manganous chloride, no precipitate is obtained; whilst by substituting the normal salt for the dichromate a copious precipitate is formed. Based on this reaction, a printing colour was prepared, which consists of a mixture of potassium dichromate, manganous chloride, and sodium acetate. On warming the solution, the sodium acetate suffers decomposition, the dichromate is neutralised, and the above-mentioned precipitate formed on the fibre. The following proportions are used :—180 grams of potassium dichromate, 850 water, 150 wheaten starch, 210 manganous chloride, and 210 sodium acetate solution (16° B). After steaming, a dark-brown colour is obtained, which resists soaps and does not attack the fibre. D. B.

**Incombustible Paper and Colours.** By G. MEYER (*Chem. News*, **48**, 164).—Samples of the author's incombustible paper, printed with his incombustible colours, were submitted to the heat of a muffle furnace and to an air-gas burner; the colours retained their brilliancy, and the paper its flexibility, suffering but a slight alteration of texture. D. A. L.

**Preparation of Waterproof Materials.** (*Dingl. polyt. J.*, **249**, 143.)—Hitherto it has been the practice to pass the tissues after treatment with linseed oil or similar oils over press cylinders. York proposes to use scraping knives, the result being the removal of all superfluous oil, without, however, expressing the oil within the pores of the tissues. D. B.

**Preparation of Artificial Stone.** (*Dingl. polyt. J.*, **249**, 142.)—For rendering stone impervious to water, Michelet and Tescher pro-



pose to treat artificially dried or burnt stone, consisting of caustic lime and clay, with tar, asphalte, or similar substances, according to the process described by Berkel for obtaining hard and weatherproof stone.

For the preparation of blocks for artificial stone and stucco, Poestges mixes gypsum with sand and lime slaked with alum water, and moistens the dry powder with glue solution and acetic acid. No sand is used when the blocks are employed for stucco. The latter can be painted with oil colours. When these are not to be used, a coating, obtained by mixing concrete mortar with dilute acetic acid, is laid on. For colouring walls evenly, the paint is made up with dilute acetic acid and sulphuric acid, which causes the colour to penetrate more deeply.

Arnold recommends to prepare bricks filled with coal-ash in the following manner:—The plastic clay is formed into the shape of a box, into the interior of which a measured quantity of ash is introduced, and the whole covered with a layer of clay. A few air-holes are made into the bricks, so that on heating the unburnt parts of the coal-ash burn away.

For the preparation of artificial grindstone, flooring slabs, &c., Simon and Petit fuse together a mixture of asphalt, sulphur, and gumlac, and add a certain amount of mineral powder. The mass is then formed into blocks by subjecting it to hydraulic pressure.

Borchert presses plastic letters and numbers out of tripoli mixed with borax and alum, after which the letters are boiled in linseed varnish and dried.

For the purpose of manufacturing porous grindstones of porcelain, according to Buchholz and Neddermann, cork cuttings are dried thoroughly and ground. They are then soaked in water, which causes them to swell strongly, and mixed with the porcelain clay. As it dries, the cork shrivels up, so that on burning irregularly formed pores are left which impart to the stone a good grinding surface.

D. B.

**Refining of Shellac.** By E. L. ANDÉS (*Arch. Pharm.* [3], 21, 291).—The crude shellac is refined in the following way:— $1\frac{1}{2}$  kilos. of soda are dissolved in 45 litres of water contained in a small boiler or kettle; 5 kilos. of the crude shellac are added in small quantities at a time. This turbid solution has the characteristic odour of shellac and a violet-red colour. The liquid is boiled for a few minutes, and, while hot, a wooden air-tight cover is cemented on the vessel. When the liquid is quite cold, the cover is removed, and the thin cake of fat which is found on the surface is separated. The solution is filtered through linen, the clear filtrate slowly decomposed with dilute sulphuric acid, and the resulting shellac washed with water until no acid reaction remains. The washed resin is now pressed and melted in boiling water, when it can be shaped with the fingers. This shellac is cooled in water containing glycerol, and, when hard, is dried. The refined shellac forms yellowish-white glistening tufts or bars which, when dry, are yellowish-brown; it should entirely dissolve in alcohol.

W. R. D.

## General and Physical Chemistry.

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**Absorption Spectrum of Blood in the Violet and Ultra-violet.** By J. L. SORET (*Compt. rend.*, 97, 1269—1270).—With a layer of 10 mm. of a 0.1 per cent. solution of blood, the absorption band in the violet is very distinct, and occupies about half the interval between G and H, its centre being at  $h$ . The ultra-violet rays are not absorbed. With a 0.166 per cent. solution the band fills the entire space between G and H, and the region beyond H is darkened; and with a 0.25 per cent. solution the band extends beyond both G and H, and there is considerable absorption in the ultra-violet. The band in the violet extends as far as the magnesium line  $\lambda = 383$ ; there is a maximum of transparence at Cd 9, then a band at Cd 12, probably due to hæmaglobin, a maximum of transparence at the magnesium line  $\lambda = 309$ ; then another band, evidently due to serum, at Cd 17, and another maximum of transparence at Cd 18, beyond which the absorption gradually increases to the end of the spectrum. The numerical results, however, vary considerably with different samples of blood.

When blood is treated with carbonic oxide, the band in the violet is slightly displaced towards the more refrangible end, and there is less absorption in the ultra-violet than with a solution of oxygenated blood of the same strength. In the ultra-violet the magnesium line  $\lambda = 383$  undergoes less absorption, and the succeeding band is also slightly displaced towards the more refrangible end. C. H. B.

**Crossed Dispersion of several Rhombic Substances.** By G. WYROUBOFF (*Jahrb. f. Min.*, 1884, 1, Ref., 4—6).—From the optical examination of a large number of rhombic bodies, the author found in  $(K, NH_4)C_4O_6 + 4H_2O$  and in the sodium ammonium sulphate and chromate,  $(Na, NH_4)SO_4 + 2H_2O$  and  $(Na, NH_4)CrO_4 + 2H_2O$ , optical anomalies similar to those observed by Des-Cloizeaux and Mallard (*Jahrb. f. Min.*, 1883, 1, 358) in prehnite, which he explains in the same way, although pseudo-symmetrical axes for these salts could not be fully established. B. H. B.

**Chemical Action of Light: Decomposition of Oxalic Acid by Ferric Chloride.** By G. LEMOINE (*Compt. rend.*, 97, 1208—1212).—Solutions of ferric chloride and oxalic acid containing a gram-molecule of the respective substances per litre were mixed in different proportions and exposed to light under comparable conditions, the carbonic anhydride which was given off being collected over glycerol and measured. Decomposition takes place in accordance with the equation  $Fe_2Cl_6 + H_2C_2O_4 = 2FeCl_2 + 2HCl + 2CO_2$  (Marchand; Jodin). The rate at which decomposition takes place depends on the intensity of the light. For a given intensity, it is at first almost uniform, but when about half the total quantity of carbonic anhydride has been given off, the rate of decomposition gradually diminishes. The greater the volume of

the liquid, the longer of course is the time before decomposition slackens. When the two solutions are separately exposed to light for several hours and then mixed, decomposition takes place more rapidly than if the solutions had not been previously insulated. Other conditions being equal, dilution with water increases the rate of change, an effect which may be due either to the partial decomposition of the ferric chloride by the water, or to a diminution in the absorptive effect of the ferric chloride due to dilution. When ferric chloride is in excess, less gas is given off than when the two substances are present in equivalent proportions; a similar effect is produced by adding ferrous chloride to the mixed solution. An excess of oxalic acid exerts an effect similar to that produced by dilution.

Water exerts little or no absorptive effect on the waves which bring about the reaction, but a screen of ferric chloride solution almost entirely prevents the decomposition. C. H. B.

**Electrochemical Energy of Light.** By F. GRIVEAUX (*Compt. rend.*, **97**, 1123—1125).—The author has investigated the effect of variations in the different conditions on the electromotive force developed by the action of light. His results will be published subsequently. C. H. B.

**Position of Amalgams of Zinc and Cadmium in Electro-potential Series.** By W. L. ROBB (*Wied. Ann.*, **20**, 798—814).—The researches of Poggendorff have established that the amalgams of zinc, tin, and lead in a sulphuric acid cell are electropositive to the non-amalgamed metal. On the other hand, the amalgams of iron and cadmium under the same conditions are electronegative to the pure metal. Henrici, on further study of this phenomenon, was led to attribute it to some secondary reaction.

This memoir contains a detailed account of some experiments on the electric relation between zinc or cadmium, and their respective amalgams, when introduced into dilute acids or solutions of salts of these metals. The E.M.F. set up was measured by Du Bois-Reymond's modification of Poggendorff's compensation method, a Daniell's cell being used as the constant. Chemically pure zinc was obtained by an electrolytic deposition on a stick of wax, which was subsequently removed. The zinc sulphate into which the plates of pure and amalgamed metal was introduced was kept neutral by the presence of zinc carbonate. The results of the experiments show that amalgamated and pure zinc, in zinc sulphate solution, only give a difference of potential equal to  $\frac{1}{1000}$  Daniell, and if the solution be kept perfectly neutral, this difference becomes infinitesimally small. But amalgamated zinc is electropositive to the pure metal when immersed in dilute acids, although this result is principally to be attributed to the formation of the salt of the metal on the surface of the zinc plate.

In the case of cadmium the amalgamated metal is electro-negative to the pure metal in cadmium sulphate solution; the difference of potential, immediately after the amalgamation, is about 0.05 Daniell, but it diminishes with the time of contact, until a certain limit is reached.

V. H. V.

**Difference of Potential of the Electric Layers of Two Liquids which are in Contact.** By E. BICHAT and R. BLONDLOT (*Compt. rend.*, **97**, 1293—1295).—The authors determine the electrical differences between two liquids, by determining the difference between each of them and a standard liquid consisting of a solution of 1 part of sodium sulphate in 24 parts of water. The electrical differences between liquids are much more constant than those between two metals, or between a metal and a liquid. This is probably due to the fact that liquids do not, like solids, retain modifications of structure caused by external forces. It would seem that the differences between two liquids are not affected by variations of temperature much greater than those which take place in an ordinary laboratory.

C. H. B.

**Electrochemical Researches on Nitrogen.** By G. S. JOHNSON (*Chem. News*, **48**, 253—257 and 264—268).—The author confirms the results of Thénard and of Berthelot as to the formation of ammonium nitrite by the action of the silent discharge on nitrogen gas in presence of aqueous vapour. He is of opinion that to render the nitrogen *active*, the gas must be perfectly dry and the electricity of high tension. The author has tried various experiments with nitrogen and hydrogen; with nitrogen, hydrogen, and oxygen; and with hydrogen and air in the Grove's gas battery. The effect of the silent discharge on tubes of nitrogen in the gas battery circuit has also been studied, when the nitrogen is found to combine completely with hydrogen in proportion of 1 vol. to 3 vols. These results and others in which currents were observed between nitrogenised and hydrogenised platinised plates, the nitrogen in the platinised plates existing apparently in an electronegative condition, are brought forward by the author as evidence of the duality of nitrogen. Other conclusions arrived at are that nitrogen and hydrogen can generate currents in Grove's gas battery which are inversely proportional to the internal resistance. The hydrogen always contracts, but if the external resistance is great, and the internal small, the volume of the nitrogen increases, but there is no combination between the nitrogen and hydrogen. When the internal and external resistance is reduced to a minimum, combination takes place, and the hydrogen contracts much more rapidly than the nitrogen expands. Ammonia has been found in the acid over which air and hydrogen, and nitrogen and hydrogen have been observed to contract.

D. A. L.

**Production of very Low Temperatures.** By L. CAILLETET (*Compt. rend.*, **97**, 1115—1117).—The production of low temperatures by allowing a jet of liquid ethylene to play upon the object to be cooled, necessitates the use of large quantities of liquid ethylene, and can only be carried on discontinuously. The author has therefore constructed an apparatus by means of which very low temperatures can be maintained for any length of time, the same ethylene being used over and over again. It consists of a copper tube bent in the form of a helix, and enclosed in a steel cylinder, beyond which the ends of the tube project. Two tubes communicate with the inside of

the cylinder and are attached to it by screw-nuts. One of these tubes is connected with the exhaust valve of the author's pump, by means of which an almost perfect vacuum can be obtained; the other is connected with a reservoir containing liquid ethylene condensed by the pump and cooled by means of methyl chloride. The liquid ethylene issues from the second tube through a stopcock of special construction, expands into the vacuum, and is removed through the first tube to the pump, by which it is again condensed and sent back through the apparatus. The substance to be cooled is contained in the copper helix enclosed in the cylinder. By means of this apparatus the author hopes to obtain large quantities of liquid oxygen, and then to use this liquid oxygen for the condensation of hydrogen.

C. H. B.

#### Heats of Formation of Lead Oxychlorides and Oxybromides.

By G. ANDRÉ (*Compt. rend.*, **97**, 1302—1303).—The oxychlorides and oxybromides were obtained by precipitating a solution of the haloid salt with the requisite amount of potassium hydroxide. The precipitates were completely dried, and then treated in a calorimeter with hydrochloric acid saturated with lead chloride, or hydrobromic acid saturated with lead bromide, as the case might be. The results were as follows:—

PbO anhydrous	+	PbCl <sub>2</sub> anhydrous, develops	+	6.52 cal.
2PbO	„	+ PbCl <sub>2</sub> „ „	+	9.24 „
3PbO	„	+ PbCl <sub>2</sub> „ „	+	10.60 „
PbO	„	+ PbBr <sub>2</sub> „ „	+	4.00 „
2PbO	„	+ PbBr <sub>2</sub> „ „	+	6.06 „
3PbO	„	+ PbBr <sub>2</sub> „ „	+	8.40 „

The addition of each equivalent of lead oxide develops approximately 2 cal.

C. H. B.

**Melting Points of Nitrates.** By E. MAUMENÉ (*Compt. rend.*, **97**, 1215—1218. See also this vol., p. 3).—Barium nitrate is decomposed when heated alone, but it can be fused with sodium nitrate without undergoing decomposition. If the two salts are mixed in equivalent proportions, there is no considerable reduction of the melting point, but when they are present in equal proportions the mixture solidifies at 322—288°, whereas the calculated melting point is 374°, that of barium nitrate being assumed to be 450°.

Lead nitrate can also be fused with an equal weight of sodium nitrate without undergoing decomposition, the fused mass forming a very transparent liquid. This mixture solidifies at 282°, the calculated melting point being 374°, that of lead nitrate being taken as 450°. A mixture of equal weights of lead, sodium, and potassium nitrates melts to a liquid which is not so transparent as the mixture of lead and sodium nitrate only. It solidifies at 259°, the calculated melting point being 358°.

Ammonium nitrate when heated alone melts at 153°, and solidifies at 135°; it begins to decompose at 212° under a pressure of 760 mm

If, however, a mixture of sodium and potassium nitrates in equal or equivalent proportions is fused and a quantity of ammonium nitrate equal to that of either of the other nitrates is thrown into it, the ammonium nitrate melts without decomposition, and the mixture forms a limpid, very transparent liquid, which deposits crystals at  $144^{\circ}$ , but appears to have a definite melting point at  $136\text{--}137^{\circ}$ , the calculated melting point being  $259^{\circ}$ . Even when the quantity of ammonium nitrate is equal to that of the other two salts together, fusion still takes place readily, and the mixture has a very definite melting point at  $122^{\circ}$ , the calculated temperature being  $233^{\circ}$ . If equal weights of sodium and ammonium nitrates are finely powdered and intimately mixed, and thrown in small quantities at a time into a heated crucible, the mixture melts to an almost transparent liquid without any decomposition or evolution of any vapours of the ammonium salt. The liquid deposits crystals at  $135^{\circ}$ , but appears to have a definite melting point at  $114.5^{\circ}$ , the calculated temperature being  $225.5^{\circ}$ . This mixture may be used as a bath for temperatures about  $120\text{--}125^{\circ}$ ; vapours of ammonium nitrate are not given off below  $200^{\circ}$ . A mixture of equal weights of potassium and ammonium nitrates does not melt quite so readily. If the salts are not very finely powdered, there is a loss of 5—10 per cent. of ammonium nitrate. This mixture melts at about  $230^{\circ}$ , the calculated temperature being  $240^{\circ}$ .

Manganese nitrate is easily decomposed when heated alone, but can be fused without decomposition in a mixture of sodium and ammonium nitrates. The mixture of the three salts may be heated to  $140^{\circ}$  without any manganese dioxide being formed. The fused mass cools to  $76^{\circ}$  without completely solidifying, and if the manganese nitrate is perfectly dry, it remains liquid even at  $15^{\circ}$ .

Strontium nitrate can in a similar manner be fused with its own weight of a mixture of sodium and potassium nitrates without alteration. The fused mixture solidifies between  $295^{\circ}$  and  $214^{\circ}$ . In the process of fusion, a small quantity of oxygen is given off, but no nitrogen oxides are evolved, and the weight of the salts is not diminished.

It is evident that oil-baths can be conveniently replaced by mixtures of alkaline and other nitrates. C. H. B.

*Note by Abstractor.*—Veley (Trans., 1883, p. 374) gives the melting point of ammonium nitrate as  $159^{\circ}$ , and the point at which decomposition begins as  $186^{\circ}$ .—C. H. B.

#### Pressure of Mercury Vapour at Ordinary Temperatures.

By H. McLEOD (*Chem. News*, 48, 251).—The vapour-tension of mercury at  $20^{\circ}$  C. is given by Hagen (*Ann. Phys. Chem.* [2], 16, 610) as 0.021 mm., by Hertz (*ibid.*, 17, 193) as 0.0013, and now by the author as 0.00574 mm. In one of the author's experiments, a glass tube, 14 mm. diameter, filled with freshly distilled mercury, was suspended in a flask, 1.9 litre capacity, which was covered with a greased glass plate, and exposed to the ordinary temperature for nine days. A small quantity of boiling nitric acid was then poured in,

which after some time was neutralised with ammonia, acidified with hydrochloric acid, and treated with hydrogen sulphide. The brown coloration thus produced was compared with a standard, from which the mercury vapour present in the flask was assumed to be 0.00009 gram. In another experiment a tube of 24 mm. diameter was employed, and after exposure for a month, the mercury found was 0.00012 gram; which calculated out gives the above tension (0.00574 mm.).

D. A. L.

**Molecular Volume of Liquid Substances.** By R. SCHIFF (*Annalen*, 220, 278—334).—In a previous paper (Abstr., 1883, 1044), the author gave the results of the determinations of the molecular volumes of a number of liquids. The present communication is chiefly taken up with the discussion of the conclusions to be drawn from these results.

In the first place, the author calls attention to the considerable differences between his observed numbers and those calculated by Kopp, and points out that these differences are due to the fact that when Kopp published his researches, little was known of the isomerism of chemical bodies and of its influence on their physical properties. Kopp's atomic constants were therefore the *means* of his various experimental numbers, whereas the author now shows that although the atomic volumes of the elements are constant for similarly constituted compounds (*i.e.*, members of a homologous series, &c.), those of multivalent elements vary when the mode of combination differs (*i.e.*, between isomeric compounds, and series, &c.).

In his comparison of results, the author uses the terms normal and secondary, with the usual meaning in the fatty series, but in the aromatic, he calls those bodies normal which contain only *one* side chain, secondary those with *two* side chains, &c. In the fatty series, the normal hydrocarbons—which have a higher boiling point—show a smaller density and higher molecular volume than the corresponding secondary compounds. In the aromatic series, the normal hydrocarbons—with a lower boiling point—show a greater density and smaller molecular volume than the secondary. The author therefore concludes that to get satisfactory results, normal compounds of the fatty series must be compared with secondary aromatic bodies and secondary fatty bodies with normal aromatic. Acting on this plan, the vol.  $C_2 = \text{vol. } H_1$  in comparable bodies. As the result of a comparison of alkyl salts of the fatty acids, the author concludes that "The molecular volumes of isomeric and analogously constituted ethers are greater the smaller the number of carbon-atoms in the acid-radical, and the greater that number is in the alcohol-radical." This result combined with Linnemann's similar deduction in regard to boiling points, may be expressed as follows:—"Of isomeric bodies composed of carbon and hydrogen, or of carbon, hydrogen, and oxygen, the one possessing the highest boiling point has also the greatest molecular volume."


On comparing the three compounds—

1. Diisobutyl, $C_8H_{18}$ . . . . .	Vol. = 184·5
2. Caprylene, $C_8H_{16}$ . . . . .	Vol. = 177·22
3. Ethyl-benzene, $C_8H_{10}$ . . . . .	Vol. = 138·95,

we have between 1 and 2 a difference of 2H, between 1 and 3 of 8H. The difference in vol. between 1 and 3 is 45·55 for 8H, and if the difference were regular, the vol. of 2 should be 173·12 or 4·08 less than found. Similarly with the three compounds—

1. Normal hexane, $C_6H_{14}$ . . . . .	Vol. = 139·7
2. Diallyl, $C_6H_{10}$ . . . . .	Vol. = 125·82
3. Benzene, $C_6H_6$ . . . . .	Vol. = 95·94

the observed vol. of 2 is 8·00 greater than the number as calculated from 1 and 3 should be. But in the first instance (caprylene) we have *one* double-linking, in the second (diallyl) *two*, and in all other similar cases the presence of a double-linking always raises the molecular volume about 4. From these results the author is led to believe that the so-called double-linking in unsaturated and in aromatic compounds cannot be of a similar nature. He is inclined to consider this fact as an argument against Kekulé's formula for benzene, and in

favour of the formula .

From the fact that the unsaturated compounds occupy a larger relative molecular volume than the saturated, he contends with Brühl that the linking in the former case is not so much a *double* as a *looser* linking than that in the latter, and that ethylene for instance would be more accurately represented by the formula  $CH_2\text{---}CH_2$  than by the formula  $CH_2 : CH_2$ . The same is the case with oxygen. When oxygen is linked to one atom of carbon only (in aldehydes, &c.), it has a much larger molecular volume than when it is linked to two carbon-atoms or one carbon- and one hydrogen-atom; and he therefore supports the formulæ  $CH_3\text{---}CH\text{---}O$  and  $HO\text{---}\overset{\overset{CH_3}{|}}{C}\text{---}O$  for acetaldehyde and acetic acid respectively. The

actual value of C seems to vary between 8 and 13, of O between 5·6 and 19. Hydrogen has a constant volume 5·6.

In conclusion, the author gives the following as a very brief summary of the most important results of his work:—

1. The specific volumes of carbon and oxygen are variable, their variation depending on that of the linking of the atoms.

2. The presence of a so-called double-linking always increases the molecular volume. This increase is 4 units for each double-linking.

3. The benzene-ring cannot contain any so-called double-linkings.

4. There are no double-linkings. Where they have hitherto been thought to exist, the linking is looser than in other cases; or in other words, a greater space exists between two atoms thus said to be doubly-linked, than in the normal state.

The following additional experimental results have been obtained since the last communication:—



Ether, Et <sub>2</sub> O .....	106·24
Propyl formate, H.COOPr.....	108·73
Isobutyl propionate, Et.COObu <sup>β</sup> ....	173·54
Methyl butyrate, Pr.COOMe.....	126·35
Methyl isobutyrate, Pr <sup>β</sup> .COOMe ....	126·43
Propyl butyrate, PrCOOPr .....	173·85
Propyl isobutyrate, Pr <sup>β</sup> COOPr.....	174·20
Isobutyl butyrate, PrCOObu <sup>β</sup> .....	197·66
Isobutyl isobutyrate, Pr <sup>β</sup> COObu <sup>β</sup> ....	198·20
Methyl valerate, BuCOOMe .....	148·32
Ethyl valerate, BuCOOEt .....	172·99
Propyl valerate, BuCOOPr .....	196·82

L. T. T.

**Dissociation of Ammonium Carbonate in Presence of an Excess of one of its Elements.** By ISAMBERT (*Compt. rend.*, 97, 1212—1215).—The author has determined the tensions of mixtures of ammonium carbamate with varying proportions of carbonic anhydride or ammonia at temperatures ranging between 34° and 52·6°, and finds a close agreement between the observed pressures and those calculated from the known excess of carbonic anhydride or ammonia on the assumption that the ammonium carbonate decomposes at the moment of volatilisation (compare Abstr., 1882, 269). C. H. B.

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## Inorganic Chemistry.

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**Specific Gravity of Liquid Oxygen.** By S. v. WROBLEWSKI (*Wied. Ann.*, **20**, 860—870).—Dumas, on the occasion of the liquefaction of oxygen by Pictet, recalled his supposition that the sp. gr. of liquid oxygen was unity; for on theoretical considerations oxygen and sulphur must possess equal atomic volumes, and therefore their sp. grs. in the liquid state will be in the ratio 1 : 2.

Pictet deduced from his experiments the values .9883 and .9787, but Offret subsequently pointed out errors in the calculation which would reduce the value to .84. However, much confidence cannot be placed in this value, for Pictet had assumed that Gay-Lussac's law held good between the wide limits of temperature + 485 and -130; moreover, it would be difficult, under the conditions of the experiment, precisely to fix the temperature of the liquefying tube, and the exact volume filled by the liquefied gas.

In order to re-determine the value for the sp. gr. of liquid oxygen, the author has made use of his apparatus, which has been described at length in a former memoir. The method is as follows:—The capillary tube of the apparatus is filled up to a certain mark with oxygen, condensed at -130°.

Then the quantity of oxygen taken  $Q_1 = v_1 d_1 + q_1 (1)$  in which formula  $v_1$  and  $d_1$  are the volume and density of the liquid oxygen,

and  $q$  the quantity remaining gaseous. If then the tube be filled up to the same mark with carbonic anhydride or nitrous oxide liquefied at  $0^\circ$ , then  $Q_2 = v_2 d_2 + q_2$  (2).

If equation (1) be divided by (2) and all referred to  $d_1$ , then

$$d_1 = d_2 \frac{v_2 Q_1}{v_1 Q_2} + \frac{q_2 Q_1 - q_1 Q_2}{v_1 Q_2};$$

but for practical purposes the latter fraction may be neglected, so that

$$d_1 = d_2 \frac{v_2 Q_1}{v_1 Q_2}.$$

The mean value of twelve concordant experiments was found to be  $\cdot 899$  at a temperature of  $-130^\circ \text{C}$  (this vol., p. 14), and the pressure of liquefaction. But Dumas in answer has suggested that the liquefied gas has a large coefficient of expansion, and if it were possible to cool the oxygen still further, the value of its sp. gr. would more nearly approximate unity. Further criticisms of Pictet are also met and discussed.

V. H. V.

**Solidification of Superfused Sulphur.** By D. GERNEZ (*Compt. rend.*, **97**, 1298—1301; 1366—1369; and 1433—1435).—Octohedral sulphur, crystallised from carbon bisulphide, was dried at  $95^\circ$  for 24 hours, placed in a graduated **U**-tube not more than 2 mm. in diameter, heated to fusion at a constant temperature **T**, during a time **℥**; then immersed in a bath at a temperature  $t$  below the melting point of sulphur. It remains in a superfused condition, and after the expiration of a time **℥'**, a crystal of prismatic or octohedral sulphur, as the case might be, was dropped down the **U**-tube. As soon as the crystal touches the surface of the liquid, the latter begins to solidify, and the time, **S**, required for solidification to extend through a constant distance (10 mm.) in the limb of the tube was observed.

For constant values of **T**, **℥**,  $t$ , and **℥'**, the time required for solidification is proportional to the distance through which solidification extends, in other words, **S** is a constant. Other conditions being equal, **S** depends on  $t$ , and is greater the nearer  $t$  approaches the melting point of sulphur. The value of **S** also depends on the values of **T**, **℥**, and **℥'** respectively. The higher the value of **℥**, *i.e.*, the longer the time during which the sulphur is kept in a state of fusion at the temperature **T**, the higher is the value of **S**. In one experiment **S** increased 8.5 times when **℥** was increased seven times, and in another **S** increased 11.58 times when **℥** was increased twelve times. It follows that **S** is very nearly proportional to **℥**. Variations in **S** caused by variations in **℥'**, the time during which the sulphur remains superfused, are very small when **T** is but slightly higher than the melting point of sulphur, but become very considerable when **T** exceeds  $170^\circ$ . In one series of experiments when **T** =  $219^\circ$ , **℥** = 5 minutes,  $t$  =  $101^\circ$ , the following values were obtained:—

<b>℥'</b> . . . . .	0 hr. 15 mins.	3 hr. 15 mins.	4 hr. 45 mins.
<b>S</b> . . . . .	23.04 seconds.	9.12 seconds.	7.70 seconds.

beyond which the value of  $S$  remained sensibly constant. Other conditions being the same, the time of solidification depends on the initial temperature  $T$ . When  $\mathcal{T} = 5$  minutes,  $t = 100.3^\circ$ , and  $\mathcal{T}' = 15$  minutes, the values of  $S$  for certain values of  $T$  are as follows:—

$T = 129.5^\circ$	$139.0^\circ$	$142.5^\circ$	$154.5^\circ$	$160.5^\circ$	$164.5^\circ$	$167.5^\circ$	$173.5^\circ$ .
$S = 0.50''$	$0.59''$	$0.70''$	$1.93''$	$5.70''$	$10.61''$	$18.08''$	$25.59''$
$T = 177^\circ$	$181^\circ$	$189^\circ$	$204^\circ$	$219^\circ$	$243^\circ$	$274^\circ$	$350^\circ$
$S = 24.98''$	$21.65''$	$21.41''$	$21.66''$	$21.43''$	$19.41''$	$18.07''$	$17.0''$

There is a sudden alteration in the value of  $S$  when  $T$  passes from  $167.5^\circ$  to  $173.5^\circ$ .\* At this last temperature,  $S$  attains a maximum, and beyond this point it very slowly diminishes as  $T$  approaches the boiling point of sulphur.

These values all refer to octohedral sulphur which is fused for the first time. If the process of fusion and solidification in prisms is repeated several times, the value of  $S$  increases, and after eight successive operations it becomes more than twelve times its original amount. In other words, the superfused liquid yields prisms more slowly when it has been formed by the fusion of prismatic sulphur than when it has been formed by the fusion of octohedral sulphur, and the time of solidification is longer the more frequently the sulphur has been solidified in the prismatic form. If, however, the sulphur is allowed to cool for some time between each successive operation, this effect is much less marked, and if the interval extends to several days, the values of  $S$  obtained at each operation are sensibly the same.

All these variations in the time of solidification of the prisms are evidently connected with changes in the specific heat of the liquid sulphur and in the heat of solidification of the prisms. The liquid sulphur at a constant temperature undergoes some modification, which depends on the duration of the action of heat, and it is evident that when the temperature of the sulphur is raised, the sulphur undergoes alterations which require time for their completion, and which do not disappear entirely until some time after the liquid has been brought to its original condition. It would seem as if the liquid in the first phase of the operation absorbed heat, which it only partially gives up in the second phase.

*Solidification of Octohedral Sulphur.*—The octohedral crystal dropped into the superfused sulphur must be very small, since the cooling effect produced by a large crystal results in the formation of prisms. In every case, the solidification of the sulphur in octohedra is very much slower than its solidification in prisms. The time of solidification ( $S$ ) varies with  $T$ ,  $\mathcal{T}$ ,  $t$ , and  $\mathcal{T}'$  as in the case of the formation of prisms. The effect of variations in  $\mathcal{T}'$  is very small, but variations in  $\mathcal{T}$  and  $T$  produce a much greater effect than in the first case. The value of  $S$  attains its maximum, 274 minutes, when  $T = 188^\circ$ , but beyond this point it decreases more rapidly than in the case of the prismatic form.

\* *Note by Abstractor.*—Between  $167.5^\circ$  and  $173.5^\circ$  the difference is 7.51 seconds for  $6^\circ$ , whereas between  $164.5^\circ$  and  $167.5^\circ$  it is 7.47 seconds for only  $3^\circ$ .—C. H. B.

It is noticeable that in the case of both the octohedral and prismatic varieties, the sulphur, at about  $170^{\circ}$ , experiences an alteration which persists whilst superfusion continues, but that if the initial temperature is much higher than  $170^{\circ}$ , although the sulphur has to cool down through this point, it solidifies almost as rapidly as if it had only been heated slightly above the melting point.

When the process of fusion and solidification in octohedra is repeated several times, the value of *S* increases, and after three successive operations becomes nearly twice its original amount, but beyond this point it remains sensibly constant, whilst in the case of the prismatic form successive fusions continually diminish the tendency to solidify.

Octohedral sulphur is repeatedly fused in a **U**-tube and caused to solidify in octohedra until it attains the condition of equilibrium represented by a constant value of *S*. It is then brought into a state of superfusion, and the liquid in one limb is caused to solidify in octohedra; that in the other in prisms. The tube is then heated for five minutes at  $129.5^{\circ}$ , kept in superfusion at  $100.5^{\circ}$  for eight minutes, and then the sulphur in *both* limbs is caused to solidify in octohedra, and this experiment is repeated three times. In one case, the successive values of *S* in the limb which had always remained in the octohedral condition were 2 mins. 20 secs., 2 mins. 20 secs., and 2 mins. 13 secs., whilst the corresponding values in the limb which had been once solidified in prisms were 7 mins. 22 secs., 2 mins. 40 secs., and 2 mins. 20 secs. It is evident that sulphur which has once been converted into the prismatic form yields octohedra much less readily than sulphur which has always retained the octohedral form, and it requires several successive fusions and solidifications to bring it into the condition of equilibrium previously mentioned. This effect is still more marked if the sulphur has been solidified in prisms several times. With respect to the octohedra, the prisms play a part opposite to that which the former play with respect to the prisms, since the formation of the prisms is most rapid in the liquid formed by the fusion of octohedra.

The stable condition into which the octohedral variety is brought by successive fusions and solidifications persists for a long time, whilst the prismatic form after similar treatment, gradually returns to its original condition. This is explained by the fact that the prismatic sulphur gradually devitrifies and passes into the octohedral variety.

The phenomena accompanying the solidification of sulphur are much more complicated than in the case of phosphorus, the difference being probably due to the fact that amorphous phosphorus is insoluble in the fused ordinary variety, whereas the different modifications of sulphur remain mixed together in the fused substance. It is important to note that  $170^{\circ}$ , the temperature which produces the maximum value of *S*, is the temperature which, according to Berthelot, produces the maximum quantity of sulphur insoluble in carbon bisulphide.

C. H. B.

**Red Sulphur of Japan.** By E. DIVERS and T. SHIMIDZU (*Chem. News*, 48, 284).—There is an orange-red variety of sulphur found

apparently in all the deposits of volcanic sulphur in Japan. It is known in the native vocabulary by a name equivalent to "massive-red-sulphur;" a specimen contained:—

Te.	Se.	As.	Mo.	Earthy matter.	Sulphur (by diff.)	
0·17	0·06	0·01	trace	trace	99·76	= 100·00.

When treated with carbon bisulphide, the arsenic remains behind as sulphide. The yellow sulphur usually associated with the red sometimes contains traces of tellurium and selenium. The two sulphurs are strikingly different in colour.  
D. A. L.

**Lead-chamber Deposit from Japanese Sulphuric Acid.** By E. DIVERS and M. SHIMOSÉ (*Chem. News*, **48**, 283).—The interest of the present paper is derived from the fact that volcanic sulphur only is employed in the Japanese works. The deposit examined came from the lead chambers as a mud; it settled down to a yellow supernatant liquid and a grey-red deposit, with many bright-yellow particles; this sediment, on elutriation, sorted itself into lead sulphate at the bottom, particles of ash and particles of sulphur next, and red particles of impure selenium at the top. The liquor was impure  $\text{H}_2\text{SO}_4$ , sp. gr. 1·15, and contained ferric sulphate and 0·37 gram tellurium and 0·15 gram selenium per litre. The sediment drained on a filter and sun-dried contained:—

Se.	Te.	S (free).	As.	Hg (free).	Cu.	Mo.
10·5	1·2	6·5	doubtful	0·016	trace	trace
PbSO <sub>4</sub> .		Ash.	H <sub>2</sub> O, H <sub>2</sub> S, organic matter, and Se <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> [very little].			
29·5		24·5	27·8		= 100·016	

The proportions of the selenium and tellurium in the acid liquor and sediment are reversed, which is due to the moist finely divided tellurium, particularly in presence of acid, oxidising more rapidly than selenium. The mercury could be extracted with nitric acid, but not with potassium cyanide solution; it was therefore considered to be uncombined. Many samples of sulphur have been examined for mercury, but this metal has never been detected. This is probably the first time molybdenum has been found in a lead-chamber deposit; it was also detected in the burner-ash. On distilling the sediment, water, sulphurous anhydride, impure sulphur, selenium, tellurium, and selenious oxide passed over, whilst crystalline galena was found among the other fixed matters in the retort. The authors have many gallons of the mud; it is therefore an average and not a special sample.  
D. A. L.

**Preparation of Oxychloride of Phosphorus from Phosphates.** By A. OGLIALORO (*Gazzetta*, **13**, 328).—The author points out that Riban's method of preparing phosphorus oxychloride by passing chlorine and carbonic oxide over heated tricalcium phosphate (Abstr.,

1883, 287) was described five years ago by Paternò (*Gazzetta*, **8**, 233). C. E. G.

**Reduction of Metallic Solutions by means of Gases, &c.** By G. GORE (*Chem. News*, **48**, 295).—A mixture of carbonic oxide and carbonic anhydride gases, passed slowly through various liquids, had the following effects. Palladium dichloride is rapidly decolorised, and all the metal is precipitated as a black powder. Platinum tetrachloride is slowly decomposed, and yields a small amount of a yellow precipitate in two or three days. In potassium iridium chloride the iridium is precipitated after some time. Lime-water contained in a leaden vessel becomes coated with a film of red oxide of lead. Silver nitrate, mercuric chloride, lead nitrate, ferric chloride, manganous chloride, potassium permanganate, chromic acid, and vanadic compounds showed no signs of reduction. A mixture of hydrogen and carbonic anhydride, also pure hydrogen, reduced a dilute solution of palladium dichloride when exposed to it, the palladium being precipitated in 24 hours. The following solutions were kept in contact with coal-gas: they each had a platinum wire immersed in them, and were in a dark place. In palladic chloride, the metal is speedily reduced, and the liquid becomes colourless in a few days. Gold chloride is also reduced, and in the course of a few days bright films of the metal float on the surface and then sink; the liquid is not wholly decomposed in three weeks. Solid gold chloride is also gradually reduced to metal. Platinic chloride only slightly decomposes in ten weeks. With silver nitrate, the decomposition starts in a few hours, but is not complete in seven weeks. Copper sulphate and ferric sulphate are not reduced. A gaseous mixture containing acetylene rapidly decomposed palladic chloride; gold chloride less quickly; platinic chloride but slightly, and potassium iridium chloride not at all. Palladic chloride, gold chloride, and platinic chloride are reduced, more or less rapidly, by amylene, petroleum, benzene, naphtha, light petroleum, mesitylene, and other similar liquids. Bright metallic films are formed between the liquids by light petroleum with palladic chloride, and by amylene with gold chloride. Paraffin and naphthalene reduce gold chloride, but not palladic chloride, whilst ozokerite acts on neither. Gold chloride is also reduced by the chlorides  $C_2Cl_2$ ,  $C_2Cl_4$ ,  $C_2Cl_6$ , and  $CCl_4$ . Benzene decolorises a solution of potassium iridium chloride in two days, whilst amylene produces no visible effect in that time. Amylene slowly precipitates mercuric chloride solution, acts rapidly on permanganate, but does not alter cupric chloride, ferric chloride, chromic acid, or its potassium salt. Benzene reduces permanganate, but not ferric chloride. Naphtha, &c., produces only a slight change in solutions of telluric, antimonious, or bismuth chloride. It is suggested that metals, found in the earth as such, may owe their origin to contact with hydrocarbons derived from organic mineral substances.

D. A. L.

**Behaviour of Silver Chloride, Bromide, and Iodide with Bromine and Iodine.** By P. JULIUS (*Chem. News*, **48**, 284).—By passing dry air saturated with bromine over silver iodide kept in a

state of fusion, the iodide is easily and completely converted into bromide after 10 minutes. In the same manner silver chloride can be converted into bromide in 1 or 2 hours. Further experiments prove that both chlorine and bromine may be expelled from their silver compounds by means of iodine vapour, although 6 to 10 hours are required to effect this change with the chloride. Hence any halogen, if supplied in excess, can expel any other halogen from its combination with silver; at least as far as chlorine, bromine, and iodine are concerned.

D. A. L.

**Recovery of Barium and Strontium Compounds.** By F. MUCK (*Dingl. polyt. J.*, 250, 91).—For the separation of barium and strontium from mixtures of their chlorides and the chlorides of sodium, calcium, magnesium, &c., the concentrated liquor is treated with a hot saturated solution of salt. Thus all the chlorides, with the exception of the sodium chloride contained in the mother-liquor, are dissolved. The salt solution is used over and over again until it is sufficiently saturated, when on cooling a mixture of barium and strontium chlorides crystallises out. By treating a cold saturated solution of these chlorides with twice the volume of hydrochloric acid, barium chloride is precipitated.

D. B.

**Cadmium Iodide.** By F. W. CLARKE and E. A. KEBLER (*Chem. News*, 48, 297—298).—The suggestion that the series of elements are developed progressively like series of compounds, such as hydrocarbons, is as yet supported only by the periodic law. Another support is now put forward under the form of isomerism, for the higher we go in a series of hydrocarbons the more frequent are the cases of isomerism; and so it is shown, that the chlorides and bromides are less prone to form isomerides than the iodides. The authors now bring forward a new example of allotropy of iodides in the form of cadmium iodide. By heating together equivalent quantities of cadmium and iodine in a sealed tube exhausted of air, or by digesting these elements under water, or by treating cadmium carbonate with hydriodic acid, or by dissolving together equivalent quantities of cadmium sulphate and potassium iodide, evaporating to dryness, extracting with alcohol and crystallising, a cadmium iodide,  $\text{CdI}_2$ , is obtained, which is white, and undergoes no change at any temperature below  $250^\circ$ , and has a sp. gr. 5.644. By dissolving cadmium carbonate in hydriodic acid and decolorising by cadmium clippings, or by dissolving cadmium in hydriodic acid, a brownish  $\text{CdI}_2$ , sp. gr. 4.626, is obtained, which, when heated at  $50^\circ$ , loses weight, and is gradually transformed into the other variety.

Unsuccessful attempts were made to prepare cadmium-lead, and cadmium-thallium iodides. Mercuric iodide dissolves freely in hot solutions of cadmium iodide, and the mother-liquor from the first crop of crystals (mercuric iodide), on standing, deposits golden laminae, which can be recrystallised from alcohol. They are anhydrous, and a partial analysis points to the formula  $\text{CdI}_2 \cdot 3\text{HgI}_2$ . There was not sufficient substance for further investigation. The authors have prepared zinc iodide from its elements, and found sp. gr. 4.666 (Bödeker found 4.696). They are now working on stannic iodide, and have found



two modifications, one darker and less soluble in benzene than the other. D. A. L.

**Atomic Weight of Aluminium.** By H. BAUBIGNY (*Compt. rend.*, 97, 1369—1371).—The sulphates of the sesquioxides are perfectly stable at  $440^{\circ}$ , and some of them, aluminium and chromium sulphates, for example, obstinately retain traces of free sulphuric acid even at this temperature.

Ammonia-alum was repeatedly crystallised, calcined until completely decomposed, the residue washed with water to remove traces of alkalis, calcined to remove organic matter, and dissolved in dilute sulphuric acid. The aluminium sulphate was twice crystallised, and then dried at  $440^{\circ}$  for a long time. Even when repeatedly powdered and heated at this temperature in a vacuum in presence of fused potash, the last traces of free acid are not expelled. If, however, the dried salt is dissolved in water and precipitated by alcohol and then carefully dried, it is obtained free from any excess of acid. The sulphate is then carefully converted into oxide by ignition. The mean result was  $Al = 27.016$  if  $S = 32$ , and  $Al = 27.064$  if  $S = 32.074$ . Mallet found  $Al = 27.02$ . C. H. B.

**Atomic Weight of Titanium.** By T. E. THORPE (*Chem. News*, 48, 251).—After some remarks on the slight experimental basis on which the greater proportion of the accepted values of the atomic weights depend, the author draws attention to the element in question. Its atomic weight was found by Rose to be 48.13 and 49.58, by Pierre 50.25; whilst Mendelejeff has adopted 48. In the present paper the author reports the results of his deduction of the atomic weight of titanium from analyses of the tetrachloride. Three independent values have been obtained based on the ratios:—(1.)  $TiCl_4 : 4Ag$ . (2.)  $TiCl_4 : 4AgCl$ . (3.)  $TiCl_4 : TiO_2$ . Value (1) was obtained by decomposing weighed quantities of the tetrachloride with water, and precipitating the chlorine with silver by Stas's modification of Gay-Lussac's method, the mean of 8 experiments giving  $Ti(H = 1) = 48.021$ . Value (2) by treating weighed quantities of the tetrachloride, decomposed with water, with excess of silver nitrate, &c., the mean of 5 experiments giving  $Ti(H = 1) = 48.018$ . Value (3) by decomposing the tetrachloride with water, evaporating the solution to dryness and strongly heating the resulting oxide, &c., gave  $Ti(H = 1) = 47.970$ . The mean of these three values is 48.003. But if the value of Ti is calculated more accurately from the aggregate weights of the tetrachloride, silver, silver chloride, and titanium oxide respectively, 48.014 is obtained for value (1), 48.016 for (2), and 47.969 for (3), and the mean is 48.000. From these observations, it would appear that the atomic weight of titanium is a simple multiple of that of hydrogen. The author is making similar observations with the tetrabromide and dioxide. D. A. L.

**Vanadates and Phosphates of the Alkali-metals.** By C. RAMMELSBERG (*Wied. Ann.*, 20, 928—943).—This paper contains an account of the methods of preparation of the various vanadates of the

alkali-metals. The results obtained are compared with those of Norblad, whose original memoir was published in Upsala, and thus has not been widely disseminated.

With the alkali-metals, vanadic acid forms a series of salts represented by the following formulæ, in which M is a monatomic metal :—

Basic vanadates.....	$\left\{ \begin{array}{l} M'_8V_2O_9. \\ M'_3VO_4, \text{ Orthovanadate.} \\ M_4V_2O_7, \text{ Pyrovanadate.} \end{array} \right.$
Neutral .....	$M'VO_3, \text{ Metavanadate.}$
Acid.....	$\left\{ \begin{array}{l} M_2V_4O_{11}, \text{ Tetravanadate.} \\ MV_3O_8 \text{ Hexvandate.} \end{array} \right.$

Others of intermediate composition have also been isolated, such as some of the ammonium compounds described at length in this memoir.  $(NH_4)_4V_{10}O_{27} \cdot 10H_2O$ , obtained by adding acetic acid to an aqueous solution of the neutral salts until a permanent red coloration is produced, forms red crystals belonging to the quadratic system, and consisting of two prisms with a regular octohedron.  $(NH_4)_3V_7O_{19} \cdot 2H_2O$ , obtained from the above acetic acid solution, is a sparingly soluble golden amorphous salt.

*Potassium pyrovanadate*,  $K_4V_2O_7$ , crystallises out when an alkaline solution of the orthovanadate is concentrated to a small bulk. On adding acetic acid to the mother-liquor from this salt, and evaporating the solution, delicate crystals of a salt of the composition  $K_{10}V_5O_{25} \cdot 7H_2O$  separate out. Similarly on the addition of acetic acid to a solution of the metavanadate, a brownish-red crystalline precipitate,  $K_4V_6O_{17} \cdot 2H_2O$ , is produced; but in the case of the ortho-salt, there is formed a red compound of composition  $K_2V_4O_{11}$ , crystallising in rhombic prisms.

*Sodium pyrovanadate*,  $Na_4V_2O_7$ , described also by Roscoe and Norblad, crystallises in tablets belonging to the hexagonal system, optically uniaxial, and giving well-defined interference bands. On the addition of acetic acid to a solution of this salt, a deep red coloration is produced, and on evaporation large red dodecahedral crystals of the composition  $Na_4V_6O_{17} \cdot 16H_2O$  separate out. These quickly effloresce in the air, to form a brighter coloured powder.

*Lithium orthovanadate*,  $Li_3VO_4$ , obtained by heating 3 mols. of lithium carbonate and 1 mol. vanadic acid, is a golden powder, insoluble in water; if lithium nitrate is substituted, there is produced lithium pyrovanadate,  $Li_4N_2O_7 \cdot 7H_2O$ , which forms white ill-defined crystals. On the addition of a trace of nitric acid to the orthovanadate, white crystals are produced of a salt,  $Li_5V_4O_{13} \cdot 15H_2O$ , sparingly soluble in water. If 1 mol. lithium carbonate and 1 mol. vanadic acid are melted together and the fusion dissolved in water, there separates from the solution the golden crystalline metavanadate,  $LiVO_3 \cdot 2H_2O$ , moderately soluble in water. If acetic acid be added to a solution of this salt, a red coloration is produced from the formation of a compound  $Li_{10}V_{12}O_{35} \cdot 30H_2O$ . From the orthovanadate, on acidification, a salt,  $Li_6V_8O_{23} \cdot 12H_2O$ , is produced, crystallising in red dodecahedra.

A brief description of other salts,  $\text{Li}_4\text{V}_6\text{O}_{17} + 15\text{H}_2\text{O}$ ,  $\text{Li}_6\text{V}_8\text{O}_{25} + 12\text{H}_2\text{O}$ ,  $\text{Li}_3\text{V}_5\text{O}_{14} + 12\text{H}_2\text{O}$ , is also given.

In the course of the preparation of the lithium salts from the carbonate and vanadic acid, the formation of a black insoluble residue was observed. This dissolves in dilute acids, and is reprecipitated by ammonia; it consists of an oxide,  $\text{V}_4\text{O}_9$ , briefly described by Berzelius, but not further investigated.

If a solution of sodium pyrophosphate be acidified with acetic acid and then evaporated, large transparent crystals of sodium dihydrogen pyrophosphate separate out.

On prolonged heating of thallium dihydrogen orthophosphate, thallium dihydrogen pyrophosphate,  $\text{H}_2\text{Tl}_2\text{P}_2\text{O}_7$ , is produced, which forms a readily soluble crystalline mass; its solution gives a white precipitate with silver nitrate.

V. H. V.

**Chromic Hydrogen Selenite.** By C. TAQUET (*Compt. rend.*, 97, 1435).—Chromic hydrogen selenite is obtained by the regulated action of nitric acid on the normal selenite. It forms irregular plates, smaller and of a deeper green colour than those of the corresponding iron compound. It is almost insoluble in water, but is soluble in acids. When heated it decomposes, at first into normal selenite and selenious acid, and finally into chromium sesquioxide and selenious acid.

C. H. B.

**Uranium Nitrate or Acetate from Residues.** By J. T. SAVORY (*Chem. News*, 48, 251).—The washed uranium or uranium ammonium phosphate is dried, powdered, and ignited. The resulting phosphate is boiled with pure strong nitric acid, and, while on the water-bath, the solution is treated with coarsely granulated tin, in quantities equal to half the weight of the phosphate. When the action ceases, the mass is evaporated to dryness, gently heated on a sand-bath, and then broken up and boiled out with successive portions of dilute nitric acid (1 to 4), leaving to settle, and filtering after each treatment. The solution of uranium nitrate is concentrated and crystallised. Uranium acetate is prepared by gently igniting the nitrate and dissolving the oxide produced in warm acetic acid, filtering and crystallising.

D. A. L.

**Oxides of Manganese.** By O. T. CHRISTENSEN (*J. pr. Chem.* [2], 28, 1—37).—The examination is one concerning the two oxides  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$ . It is well known that braunite,  $\text{Mn}_2\text{O}_3$ , differs in crystalline form from the other oxides  $\text{R}_2\text{O}_3$ , as also does hausmannite,  $\text{Mn}_3\text{O}_4$ , from the oxides  $\text{R}_3\text{O}_4$ , and on account of this difference these two oxides of manganese have been expressed by other formulæ, viz.,  $\text{MnO}$ ,  $\text{MnO}_2$  and  $2\text{MnO}$ ,  $\text{MnO}_2$ , which are capable of explaining certain anomalies, and receive strong confirmation from the observations of Forchhammer, Berthier, and Turner, that when treated with dilute hydrochloric or sulphuric acids, or with nitric acid, they are decomposed into their constituents of which the manganous oxide goes into solution, while the manganese dioxide remains undissolved. Manganic oxide was prepared from the dioxide by ignition in a current of

oxygen, the dioxide being prepared from manganous nitrate. The pure manganic oxide, treated with boiling dilute nitric acid (17 per cent.), or boiling dilute sulphuric acid (1 vol.  $\text{H}_2\text{SO}_4$  to 9 vols.  $\text{H}_2\text{O}$ ), is decomposed in such a way that exactly one half of the manganese goes into solution, the other half remaining as the dioxide. From 100 parts of the manganic oxide containing 69·35 parts of manganese were obtained residues containing respectively 34·63, 34·58, and 34·62 of manganese. But there are reasons why these oxides should be expressed as  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$ , and not as  $\text{MnO}$ ,  $\text{MnO}_2$  and  $2\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$ . A similar behaviour is shown by cuprous oxide, which, by the action of hydrochloric acid, yields cupric chloride and metallic copper. With oxygen and chlorine, iron has no tendency to form such compounds as  $\text{FeO}$  and  $\text{FeCl}_2$ . But in combination with sulphur it is otherwise; here  $\text{FeS}_2$  corresponds to  $\text{MnO}_2$ , and the sulphide  $\text{Fe}_2\text{S}_3$  is decomposed by acids, giving rise to the production of a ferrous salt and  $\text{FeS}_2$ . Again, the hydrate,  $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , may be compared both in constitution and behaviour with acids to oxalic acid, the first yielding the monoxide and dioxide of manganese and water when treated with  $\text{HNO}_3$  of 30—40 per cent., the latter monoxide and dioxide of carbon and water on treatment with strong sulphuric acid. Thus it is evident that the behaviour of manganic oxide with acids is not a proof of the correctness of the formula  $\text{MnO}$ ,  $\text{MnO}_2$ .

Manganic oxide treated with acetic acid of from 15 to 65 per cent. was scarcely acted on, only 1—1·3 per cent. being dissolved. Manganoso-manganic oxide is acted on by dilute acetic acid of 30 per cent. as though it were  $2\text{MnO}$ ,  $\text{MnO}_2$ , approximately one-third remaining undissolved; but with stronger acid less, and with glacial acetic acid only 1·6 per cent. of manganese goes into solution. The acid solutions in the last case were of a brown colour, the insoluble residue was found to be pure  $\text{Mn}_3\text{O}_4$ , and hence the dissolved portion contained manganese and oxygen in the ratio 3 : 4. The above manganoso-manganic oxide had been ignited; a sample of the hydrated oxide prepared by Moissan's method was more readily acted on, and gave a brown solution which, on standing, deposited a crystalline deposit; this was found to have the composition  $\text{Mn}_2\text{O}_3 \cdot \text{Ac}_2 + 4\text{H}_2\text{O}$ , and is therefore the normal manganic acetate. Thus, by treatment with acetic acid, manganoso-manganic oxide (hydrated) yields manganic acetate which crystallises out, and manganous acetate which remains in solution. Strong sulphuric acid acts in a similar manner, manganous and manganic sulphates being formed *without* evolution of oxygen. Thus whilst with dilute acids  $\text{Mn}_3\text{O}_4$  behaves as  $2\text{MnO}$ ,  $\text{MnO}_2$ , with strong acids it behaves as  $\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$ .

The author then proceeds to show that manganic oxide really belongs to the group of sesquioxides, and that it forms salts resembling the ferric salts.

II. *Manganic acetate* is obtained by the action at the ordinary temperatures of 200 c.c. glacial acetic acid on 5 grams of the air-dried oxide. After about eight days, the whole is heated and filtered; on adding 2 c.c. of water to the filtrate and allowing it to remain for some time, it deposits the salt in brown crystals. The crystals are

soluble in hot glacial acetic acid; the solution, and also the dry salt, are decomposed by excess of water, and they afford a number of characteristic reactions. When it is mixed with strong sulphuric acid, and water is added gradually, a deep red solution is obtained, which deposits Fremy's salt,  $\text{MnO}, \text{MnO}_2, 4\text{SO}_3 + 9\text{H}_2\text{O}$ . Heated to a red heat, it leaves manganic oxide. The analytical numbers agree with the formula  $\text{Mn}_2\text{O}_6\text{Ac}_6 + 4\text{H}_2\text{O}$ .

*Manganic phosphate* is formed by decomposing the acetate with phosphoric acid, but more conveniently by adding a concentrated solution of manganous oxide in nitric acid to a hot aqueous solution of phosphoric acid. The salt soon begins to form, with evolution of nitrous fumes; it is washed with water and dried at  $100^\circ$ . It is a greenish-grey powder. It is scarcely acted on by dilute acids; strong sulphuric acid converts it into the sulphate. Analyses show it to be  $\text{Mn}_2\text{O}_6(\text{PO})_2 + 2\text{H}_2\text{O}$ .

*Manganic arsenate* is prepared similarly to the phosphate. It is a rather dark grey powder. Analyses show it to be  $\text{Mn}_2\text{O}_6(\text{AsO})_2 + 2\text{H}_2\text{O}$ .

*Manganic sodium pyrophosphate*.—By mixing a solution of the acetate in glacial acetic acid, with sodium pyrophosphate solution, the salt is deposited as a red crystalline precipitate. It is also prepared by treating manganic oxide with concentrated hydrochloric acid, and filtering this solution into a solution of sodium pyrophosphate in large excess. The salt is dried at the ordinary temperature. It easily loses its water of crystallisation. Manganese dioxide may also be used for this preparation, and this supports the statement (Pickering) that when treated with hydrochloric acid the dioxide does not yield the tetra- but the sesqui-chloride. From analyses the formula  $\text{Mn}_2\text{Na}_2(\text{P}_2\text{O}_7)_2 + 10\text{H}_2\text{O}$  is deduced; it therefore resembles the corresponding iron salt, and belongs to the series of salts examined by Jørgensen and Wallroth. From these experiments, it is evident that the salts described are in reality manganic salts and analogous to the ferric salts, that is, they contain the hexavalent double atom  $\text{Mn}_2$ ; the author would regard Fremy's sulphate as an acid salt, viz.,  $\text{Mn}_2\text{H}_2(\text{SO}_4)_4 + 8\text{H}_2\text{O}$ .

III. Manganese dioxide is slowly converted into the sesquioxide when heated, then into manganoso-manganic oxide, and finally into manganous oxide. That the formation of this last oxide is not due to the action of reducing gases is shown by the same results being obtained when the crucible lid, provided with an outlet tube, is cemented on. At high temperatures therefore the monoxide is the most stable of the manganese oxides; but nevertheless under other conditions there is a great tendency for manganese to behave, not as a dyad but as a tetrad element when combined with oxygen. Thus when manganoso-manganic oxide, prepared by gently heating the dioxide in hydrogen, is heated in the air it absorbs oxygen, and when boiled with an ammonium chloride solution a small quantity of manganous chloride is formed.

The manganoso-manganic oxide prepared by Otto's method also absorbs oxygen; even below  $100^\circ$  and at  $300^\circ$  it is oxidised further than to the sesquioxide. Otto states that the oxide is not decom-

posed by boiling with ammonium chloride solution, but from the author's experiments it is seen that this preparation always contains more oxygen than it should do; if, however, the boiling with ammonium chloride solution be not repeated, but performed only once, then the excess of oxygen contained is very small. This pure preparation is acted on by ammonium chloride solution. H. B.

**Phosphides of Iridium and Platinum.** By F. W. CLARKE and O. T. JOSLIN (*Chem. News*, 48, 285).—Iridium for pen-points is prepared from iridosmin, by heating the ore to whiteness and throwing phosphorus upon it; fusion takes place at once, and the excess of phosphorus is removed by subsequent treatment with lime. Iridosmin was found to contain 15·38 per cent. osmium. The "fused iridium" gave on analysis: Ir, 80·82; Os, 6·95; P, 7·09; Ru and Rh, 7·20 per cent.; three other determinations of phosphorus yield an average of 7·61 per cent. The fused iridium appears to be a phosphide of the formula  $\text{Ir}_2\text{P}$ , which would require 7·43 per cent. of phosphorus. The sample analysed is impure, owing to the impurities in the iridosmin. When 15·42 grams platinum were heated to whiteness, and 20 grams ordinary phosphorus thrown upon it, fusion at once took place, and when the excess of phosphorus was burnt off a bright silver-white button was obtained, weighing 19·4663 grams. From this synthesis the numbers following are obtained:—Pt 79·21 and P 20·79 per cent.

A portion of this phosphide—about 71·21 per cent.—is soluble in aqua regia, the insoluble portion can be dissolved by fusion with sodium nitrate and caustic soda, and subsequently boiling with aqua regia; on analysis it proved to be a definite phosphide of the formula  $\text{PtP}$ , whilst the soluble portion agreed approximately with the formula  $\text{PtP}_2$ . By re-calculating the analysis of the two separate portions, so as to express the composition of the original phosphide, the following results are obtained:—

	Found analysis.	Found synthesis.	Calculated for $\text{Pt}_3\text{P}_5$ .
Pt .....	79·39	79·21	79·05
P .....	20·87	20·79	20·95
	<hr/> 100·26	<hr/> 100·00	<hr/> 100·00

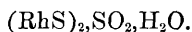
The ratio between the soluble and insoluble phosphides agrees well with the equation  $\text{Pt}_3\text{P}_5 = \text{PtP} + 2\text{PtP}_2$ , especially if some allowance is made, as the boiling with aqua regia was rather prolonged, and therefore some of the  $\text{PtP}$  was most likely dissolved as well as the  $\text{PtP}_2$ .

When the  $\text{Pt}_3\text{P}_5$  is heated in a muffle until the weight is constant, the product is malleable, and readily soluble in aqua regia. It contains 7·36 per cent. of phosphorus, the exact amount required by  $\text{Pt}_2\text{P}$ , this then is the fourth platinum phosphide, and is analogous in composition to the "fused iridium." Some platinum phosphides have been prepared before, but have never been regularly analysed.

D. A. L.

**A Compound of Rhodium.** By H. DEBRAY (*Compt. rend.*, 97, 1333—1335).—When finely divided rhodium is fused with 20 or 30

times its weight of iron pyrites, a regulus is obtained, which on treatment with hydrochloric acid, leaves a residue of blackish scales with a semi-metallic appearance. This substance whilst moist dissolves completely in dilute nitric acid, forming a highly coloured solution; but if dried it undergoes some alteration and becomes insoluble in dilute nitric acid, but is soluble in strong nitric acid if the drying has not been effected at too high a temperature. When dried at  $100^{\circ}$  in air or in a vacuum, it contains 9.6 per cent. of water and 8.6 per cent. of oxygen, which form an essential part of its constitution. Water and sulphurous anhydride are given off on heating, and a residue is left which consists of rhodium sulphide containing a trace of iron, and is insoluble in aqua regia. The composition of the black substance may be represented by the empirical formula



It is evident that the action of iron pyrites on rhodium at a high temperature can give rise only to the formation of rhodium sulphide, and it follows that the new compound is formed when the regulus is treated with hydrochloric acid. It would seem as if rhodium sesquisulphide was oxidised and hydrated, thus:  $\text{Rh}_2\text{S}_3 + \text{O}_2 + \text{H}_2\text{O} = (\text{RhS})_2, \text{SO}_2, \text{H}_2\text{O}$ . A similar reaction takes place when dilute nitric acid acts on lead holding a small quantity of rhodium in solution. A finely divided black residue is obtained, which contains rhodium, lead, and about 15 per cent. of nitrous compounds. This substance decomposes with explosion when heated, giving off nitrogen oxides, and it is readily soluble in warm concentrated sulphuric acid, which does not attack rhodium.

The nitric acid solution of the new compound does not contain rhodium sulphate alone. Part of the sulphur is not precipitated by a barium salt, and only a portion of the rhodium is reduced by formic acid.

It seems probable that the amorphous substances previously obtained in a similar manner from other platinum metals have a similar composition.

C. H. B.

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### Mineralogical Chemistry.

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**Iron containing Nickel from Sanarka, in the Ural Mountains.** By C. GREWINGK (*Jahrb. f. Min.*, 1884, 1, Ref., 29—30). —In the gold stream-work near Troizk, a piece of iron weighing 3·5 grams has been found. It is possibly of meteoric origin. It is of a steel-grey colour.  $H. = 4-5$ ; sp. gr, 7·83. It is entirely soluble in hydrochloric acid, and contains about 2 per cent. of nickel.

B. H. B.

**Action of Fused Magmas on Various Minerals.** By C. DOELTER and E. HUSSAK (*Jahrb. f. Min.*, 1884, 1, Mem., 18—44).—These



researches were undertaken to imitate and, if possible, to throw some light on the various contact phenomena brought about by the action of magmas in a state of igneous fusion. The minerals which were subjected to the action of a fused magma were:—olivine pyroxene, hornblende, biotite, felspar, quartz, garnet, dichroite and zircon. Finely powdered basalt, andesite, or phonolite, was fused in a porcelain crucible, and the above-mentioned minerals were dipped into the molten mass, and subjected for some time to its action. In several cases the minerals were placed in the powdered rock and fused. No alteration of the porcelain crucible took place.

*Pyroxene*, when subjected to the action of a fused magma, dissolves at the edges, or is converted into a fibrous or granular aggregate. The conversion into augite crystals, which is observed when bronzite is subjected to the action of fused phonolite, seems to be due not to the heat alone, but also to chemical action. Fused monoclinic augite separates out from the magma in the same state as before, whilst rhombic augite often separates out as monoclinic augite.

*Hornblende*.—Where the magma has acted on the hornblende, solution of the edges occurs. This so-called opacite edge may be observed in many younger eruptive rocks. If the action be greater, a more or less perfect change of the hornblende into augite takes place. It is remarkable that where the fusion with the magma is imperfect, the form of the hornblende remains unchanged, but on examination under the microscope, it is found to consist of an aggregate of small augite columns and magnetite. Similar "pseudo-crystals" of augite and magnetite after hornblende frequently occur in basaltic rocks, but up to the present time have never been regarded as being caused by contact action.

*Olivine*.—The author's experiments confirm the view of Roth and Rosenbusch that olivine was the first mineral that separated out of the basaltic magma.

*Garnet* is altered by fusion in basaltic magmas; these alterations are of two kinds. In one case a new formation of minerals was not observed: the alteration being confined to a peculiar cloudiness, suggestive of Schrauf's kelyphite, granulation and slight formation of opacite. In other cases chemical changes undoubtedly take place; spinel crystals and green augite occurring as products of the alteration.

B. H. B.

**Mineralogical Notes.** By A. BRUN (*Jahrb. f. Min.*, 1884, 1, Ref., 23—24).—1. *Perowskite* from Rympfischwäng near Zermatt:

TiO <sub>2</sub> .	FeO.	CaO.	Total.	Sp. gr.
59·39	0·91	39·80	100·10	3·974

2. *Desmine* from the Viesch Glacier:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	H <sub>2</sub> O.	Total.
57·44	15·43	8·71	18·03	99·61

3. *Albite* from the moraine of the "Glacier de Trelatete" (Mt. Blanc):

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Na <sub>2</sub> O.	Total.
68.57	19.67	11.90	100.14

4. *Orthoclase* from the protogine-gneiss of Mt. Blanc :

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	FeO.	Total.
66.02	19.48	0.88	7.84	5.60	trace	99.82

5. *Ripidolite* from Mt. Blanc :

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	H <sub>2</sub> O.	Total.
26.60	18.02	29.67	15.85	9.98	100.12

6. *Pinite* from Auvergne. A number of water determinations were made (1.99; 2.46; 2.75; 3.48 per cent. H<sub>2</sub>O) showing that the percentage of this constituent increases with the decomposition of the dichroite and its decrease in hardness.

7. *Borocalcite* from Chile. After the removal of Na<sub>2</sub>SO<sub>4</sub> and NaCl by washing with water, the residue gave :—

CaO.	Na <sub>2</sub> O.	H <sub>2</sub> O.	B <sub>2</sub> O <sub>3</sub> .	Total.
14.69	1.87	34.95	(48.49)	100.00

from which the formula, 3Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> + 9Ca<sub>3</sub>B<sub>14</sub>O<sub>22</sub> + 19H<sub>2</sub>O, is deduced.  
B. H. B.

**Corrosion Faces of Fluorspar.** By F. J. P. v. CALKER (*Jahrb. f. Min.*, 1884, 1, Ref., 7—8).—The specimens examined came from Brienz (Switzerland). They were aggregates of sea-green crystals of the combination  $\infty O \infty . \infty O n$ ; the faces however, were all greatly corroded. The corroded planes formed small four-sided depressions with their lateral edges parallel with the combination edges of  $\infty O \infty , O$ . The corrosion plane was determined to be  $\frac{1}{2} O \frac{1}{2}$ . Larger depressions also occur which exhibit the form  $\infty O \frac{1}{2}$ .  
B. H. B.

**A Peculiar Kernel Structure in Fluorspar.** By F. J. P. v. CALKER (*Jahrb. f. Min.*, 1884, 1, Ref., 7).—On the cubical faces of small violet crystals of fluorspar ( $\infty O \infty . \frac{1}{3} O \frac{1}{3} . O$ ) which filled drusy cavities in zinnwaldite, a finely defined square was always observed. The sides of the square were parallel to the combination edges,  $\infty O \infty : O$ , and, when examined under the microscope, proved to consist of irregular violet patches, whilst the interior and exterior of the square proved to be colourless. This appearance is explained as being due to kernel structure. A colourless crystal,  $\infty O \infty : O$ , or,  $\infty O \infty : m O m$ , must have first been formed, then the violet pigment and on this the planes  $\frac{1}{3} O \frac{1}{3}$  and  $O$ .  
B. H. B.

**Pyrostilpnite from St. Andreasberg.** By O. LUEDECKE (*Jahrb. f. Min.*, 1884, 1, Ref., 11—12).—The pyrostilpnite or fire-blende from St. Andreasberg gave the following results on analysis :—

Ag.	Sb.	S.	Total.
59.435	22.302	18.113	99.850

The formula is  $\text{Ag}_3\text{SbS}_3$ , which is also the formula of pyrrargyrite, so that the compound is dimorphous. The crystallographical examination shows that the mineral is monoclinic,  $a:b:c = 0.3547:1:0.1782$ ;  $\beta = 90^\circ 0'$ . The following forms were observed:  $-4\text{P}_4$ ,  $4\text{P}_4$ ,  $\infty\text{P}$ ,  $\infty\text{P}_2$ ,  $\text{P}\infty$ ,  $-\text{P}\infty$ ,  $-2\text{P}_2$ ,  $\infty\text{P}_4$ ,  $0\text{P}$ ,  $\infty\text{P}\infty$ . B. H. B.

**Relations between the Crystalline Form and Chemical Composition of Arsenical Iron Pyrites.** By ARZRUNI and BAERWALD (*Jahrb. f. Min.*, 1884, **I**, Ref., 10—11).—The authors have examined a number of specimens of crystallised arsenical pyrites to determine whether the angle of the prism, or, what amounts to the same thing, the ratio of the axes  $a$  and  $b$ , bears a fixed relation to the percentage of sulphur.

If the results be arranged in a series according to the value of the axis  $a$ , and if the lengths of this axis and the sulphur-percentage of the two end members be compared, it will be seen that a difference of 0.01872 in the axis  $a$  corresponds to a difference of 4.42 per cent. of sulphur, or, in other words, an increase of 0.00001 in the axis  $a$  represents an increase of 0.00236 in the percentage of sulphur. Hence, if the axis  $a$  be given, the percentage of sulphur may easily be calculated, and *vice versa*, always supposing that the difference in the length of the axis  $a$  stands in direct proportion to the percentage of sulphur.

In the following table the sulphur percentage has been thus calculated, and compared with the value actually obtained on analysis:—

Locality.	Axis $a$ .	Sulphur found.	Sulphur calculated.
Reichenstein.....	0.67092	18.051	—
Sangerberg .....	0.67052 (?)	18.290	17.957 (?)
Hohenstein .....	0.67725	19.585	19.547
Ehrenfriedersdorf .....	0.67811	19.761	19.748
"Plinian" .....	0.67960	20.080	20.099
Sala .....	0.68066	20.410	20.350
Joachimsthal .....	0.68215	20.520	20.701
Freiberg .....	0.68279	20.831	20.852
Binnenthal .....	0.68964	22.472	—

From the above results it is evident that the crystal form is dependent on the chemical composition. The crystals from Sangerberg do not follow the law; the measurements of the angles being inexact. If the sulphur in these analyses be regarded as being in the form of  $\text{FeS}_2$ , the remainder of the iron must then bear a varying ratio to the arsenic, viz., 1:1.669 to 1:2.088. If, however, the ratio be taken as 1:2, then 0.7743 to 1.1956  $\text{FeAs}_2$  would be required for one molecule of  $\text{FeS}_2$  in the various analyses. No explanation can be given of the variable percentage of sulphur in arsenical pyrites; it is, however, clear that the theory that the arsenical pyrites are isomorphous mixtures of  $\text{FeS}_2$  and  $\text{FeAs}_2$ , is not allowable. B. H. B.

**Identity of Spathiopyrite and Safflorite.** By F. SANDBERGER (*Jahrb. f. Min.*, 1884, 1, Mem., 69—70).—L. McCay points out the identity of the *safflorite* of Breithaupt, with the *spathiopyrite* described by the author in 1868. The author now finds that the sp. gr. of the mineral is 7.1 and not 6.7 as originally stated; there can be no doubt, therefore, that the two minerals are identical. B. H. B.

**Hæmatite from the Hargita-Gebirge.** By A. SCHMIDT (*Jahrb. f. Min.*, 1884, 1, Ref., 12—13).—The crystals occur in fissures of an amphibole andesite. The chemical analysis gave:—

Fe.	O.	Total.
70.27	29.43	99.70

On the tabular crystals the following forms were observed: 0R,  $\infty$ P2,  $\frac{4}{3}$ P2, R,  $-2R$ ,  $-\frac{1}{2}R$ ,  $-\frac{1}{2}R3$ . The nearest analogue to the Hargita crystals are those of Biancavilla (Abstr., 1881, 237).

B. H. B.

**Crystal of Stephanite from Wheal Newton.** By W. J. LEWIS (*Jahrb. f. Min.*, 1884, 1, Ref., 7).—A crystal of stephanite has been found, for the first time in England, at Wheal Newton, in Cornwall. It was associated with chalybite and quartz. The observed planes were:  $\infty P\infty$ ,  $\infty P\infty$ , 0P,  $\infty P$ ,  $\infty P\frac{1}{2}$ , P,  $\frac{1}{2}P$ ,  $\frac{1}{3}P$ ,  $\frac{2}{3}P\infty$ ,  $P\infty$ ,  $2P\infty$ ,  $2\frac{1}{2}P4$ ,  $\frac{3}{4}P\frac{1}{2}$ ,  $P\infty$ ,  $\frac{8}{5}P\frac{1}{5}$ .

B. H. B.

**Production of Zeolites in the Cold.** By F. GONNARD (*Jahrb. f. Min.*, 1884, 1, Ref., 28).—Fournet in his "Géologie Lyonnaise" (p. 658) describes the occurrence of zeolites in cavities of a lava from the volcano of Louchadière. These zeolites are found only in cavities below the usual river-level, and as they are partially filled with water, Fournet inferred that the zeolites were here formed in the cold under the influence of river water. From a closer examination of these "zeolites," the author found that they consisted solely of aragonite.

B. H. B.

**Vaugnerite at Irigny (Rhône).** By F. GONNARD (*Compt. rend.*, 97, 1155—1157).—The granite in a large quarry below Irigny is traversed by an almost vertical dyke about 10 meters in thickness. The material of which the dyke is composed is highly micaceous, and has undergone considerable disintegration; it very closely resembles the *vaugnerite* which Fournet found near Vaugneray (Rhône), and which Deluse regards as a micaceous diorite. The altered rock contains three principal constituents; mica, in blackish elongated plates; feldspar more or less kaolinised, and forming small white masses which surround an unaltered pinkish nucleus; and numerous flattened citron-yellow hexagonal prisms, with an earthy fracture, in all probability produced by the alteration of hornblende. The less decomposed portions of the *vaugnerite* contain brown crystals of sphene of the Arendal type, and the rock also contains prismatic needles of apatite, which are especially abundant, disseminated in the altered

crystals of hornblende. The proportion of apatite, however, is not sufficient to give the rock any industrial value. C. H. B.

**Formation of Bauxite and Gypsum.** By S. MEUNIER (*Compt. rend.*, 97, 1444—1446).—When white marble is left in contact with a solution of aluminium sulphate for a long time, carbonic anhydride is very slowly given off, and the marble becomes covered with a white mamillary crust, which contains aluminium, calcium, sulphuric acid, and water. This crust is a mixture of several substances, viz.:—(1.) An amorphous substance soluble in cold dilute potash. It probably contains aluminium hydroxide, but its solution contains sulphuric acid, and it may therefore be a basic sulphate. (2.) Small acicular crystals of gypsum. (3.) Transparent, brilliant, relatively bulky spheres and ellipsoids, sometimes 0.1 mm. in diameter. They are frequently connected together, and enclose crystals of gypsum. Mixed with these bodies are numerous crystals derived from the regular octohedron, a combination of octohedron and cube being one of the most frequent forms. These crystals occur only in small quantity. They contain sulphuric acid, calcium, and aluminium, and may perhaps be regarded as a kind of alum; they dissolve slowly in cold water and immediately in boiling water, but are insoluble in alcohol.

This experiment throws little light on the formation of bauxite, but it affords a clue to a probable mode of formation of gypsum, especially when it is remembered that the latter is sometimes found associated with websterite (aluminium sulphate). C. H. B.

**New Selenium Minerals from Cacheuta.** By E. BERTRAND (*Jahrb. f. Min.*, 1884, 1, Ref., 9—10).—Molybdomenite (selenite of lead), cobaltomenite (selenite of cobalt), and selenic acid, are found at Cacheuta, La Plata, associated with chalcomenite ( $\text{SeCuO}_3 \cdot 2\text{H}_2\text{O}$ ) recently described by Des-Cloizeaux (*Abstr.*, 1883, 31). Molybdomenite forms rhombic lamellæ with pearly lustre. The crystals of cobaltomenite are monoclinic. They are extremely small, and have the colour of erythrine. Selenic acid occurs as very fine white needles, and is due to the decomposition of the molybdomenite.

B. H. B.

**Thorite of Arendal.** By L. F. NILSON (*Jahrb. f. Min.*, 1884, 1, Ref., 8).—In 1876 Nordenskiöld discovered, at Arendal, a crystallised silicate containing 50 per cent. Th and 10 per cent.  $\text{UO}_2$ . The author is of opinion that this mineral contains uranium in the form of  $\text{UO}_2$ , corresponding to the  $\text{ThO}_2$ , and supposes that these two oxides replace each other in thorite in variable proportions. The mineral is thus only a variety of thorite rich in uranium, and not a distinct mineral.

B. H. B.

**Hübnerite from the Pyrenees.** By E. BERTRAND (*Jahrb. f. Min.*, 1884, 1, Ref., 14).—The author found the pure manganese wolframate, hitherto only known in Nevada, in the dialogite of Adervielle, Hautes Pyrénées, together with friedelite and manganese-blende. The forms,  $\infty\text{P}$ ,  $\infty\text{P}\infty$ ,  $\infty\text{P}\infty$ , were observed. The crystals were transparent and of a rutile-red colour.

B. H. B.

**Note on the Optical Properties of Nevada Hübnerite.** By A. DES-CLOIZEAUX (*Jahrb. f. Min.*, 1884, 1, Ref., 14—15).—Contrary to the author's theory, according to which the optical axes of the natural hübnerite lie in  $\infty P\infty$ , Groth and Arzruni (*Pogg. Ann.*, 1873, 235) found in artificial crystals the axial plane perpendicular to  $\infty P\infty$ . On a further examination of the natural crystals, the author found that the theory of Groth and Arzruni is correct.

B. H. B.

**Jadeite from Thibet.** By E. COHEN (*Jahrb. f. Min.*, 1884, 1, Mem., 71—73).—Microscopic examination of a fragment of jadeite presented to the author by Damour proved it to be a member of the pyroxene-group. The analysis gave the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Na <sub>2</sub> O.	Total.
59·17	22·58	1·56	2·68	1·15	12·93	100·07

The close resemblance of this mineral to the augite from a South African eclogite (*Jahrb. f. Min.*, 1879, 864) induced the author to suppose that the silicate, Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, 4SiO<sub>2</sub>, was present, and with this hypothesis to calculate the analysis of the jadeite, as well as several of Damour's older analyses. He, however, invariably obtained a considerable excess of SiO<sub>2</sub>, when the remaining constituents were regarded as MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and RO, SiO<sub>2</sub>, as in the African pyroxene.

B. H. B.

**Dichroite from Asama-Yama.** By E. HUSSAK (*Jahrb. f. Min.*, 1884, 1, Ref., 76—77).—Among the fragments ejected from the Japanese volcano, Asama-Yama, the author found normal andesite lapilli, andesite lapilli with enclosures of a white, finely granular rock containing dichroite, and the latter rock also occurring independently among the ejected fragments. Ejected matter containing dichroite, and almost entirely free from augite and magnetite, gave on analysis the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	CaO.
74·65	15·32	2·34	0·26	1·96
MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Ignition.	Total.
0·79	1·42	4·11	0·45	101·30

The dichroite forms columnar crystals of the combination  $\infty P$ ,  $\infty P\infty$ ,  $0P$ , and, strange to say, is always developed as twin crystals along  $\infty P$ , in the way frequently met with in the rhombic carbonates of the aragonite series.

B. H. B.

**Twin Crystals of Dichroite from the Laacher See.** By A. v. LASSAULX (*Jahrb. f. Min.*, 1884, 1, Ref., 77—79).—The author describes ejected matter from the Laacher See very rich in dichroite. It is a microscopic mixture of glassy felspar, dark violet dichroite in large badly-developed six-sided columns ( $\infty P$ ,  $\infty P\infty$ ,  $0P$ ), corundum, biotite, and pleonast. As in the case of the dichroite from the Japanese

volcano, Asama-Yama, the dichroite, in which the plane of the optical axes is parallel to  $\infty P\infty$ , is developed as twin crystals along  $\infty P$ .

B. H. B.

**Culm Conglomerate, containing Variolite, at Hausdorf, in Silesia.** By E. DATHE (*Jahrb. f. Min.*, 1884, 1, Ref., 73—74).—Of all the specimens of variolite examined, only one, which unfortunately was not analysed, proved to be a true variolite, that is, an endomorph contact-product of diabase. All the others resemble the true variolites in external appearance only. They consist principally of albite, quartz, muscovite, and iron pyrites. The ground-mass is a mixture of quartz and albite with finely-disseminated chlorite. Analyses of two specimens are given:—

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Na <sub>2</sub> O.
I ..	72·23	0·20	13·90	1·86	0·57	0·23	0·88	2·71
II ..	75·22	—	14·32	1·86	0·57	0·13	0·53	3·62

	K <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	CO <sub>2</sub> .	SO <sub>3</sub> .	H <sub>2</sub> O.	Organic matter.	Total.	Sp. gr.
I ..	3·57	0·17	0·04	0·17	1·97	0·04	99·54	2·691
II ..	3·91	—	—	—	1·29	—	100·11	2·682

B. H. B.

**Green Mica in the Quartzites of Ouro Preto (Brazil).** By H. GORCEIX (*Jahrb. f. Min.*, 1884, 1, Ref., 20).—Micas with a small percentage of chromium are widely distributed in the quartz mica schists, containing quartzites and topaz, of the province of Minas Geraës. The author has found a mica rich in chromium in a quartzite belonging to the same horizon at Ouro Preto. This bright green translucent mica (sp. gr. 2·78) has the following composition:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Ignition.	Total.
46·5	37·2	0·9	0·8	7·9	1·3	4·7	99·3

Unlike the green mica from the Ural Mountains (Abstr., 1883, 1066) here only a small portion of the alumina appears to be replaced by chromium, and magnesia is present to a very small extent.

B. H. B.

**New Mineral from Barbin near Nantes.** By A. DES-CLOIZEAUX (*Jahrb. f. Min.*, 1884, 1, Ref., 8—9).—A new silicate of aluminium, iron, and calcium occurs, together with quartz and apatite, in cavities in a pegmatite rock at Barbin, near Nantes. The crystals are rhombic and occur in the form of colourless rectangular plates 0·75 mm. long and 0·5 mm. broad. The mineral is probably identical with that from Petit-Port described by Bertrand (*Jahrb. f. Min.*, 1881, 1, 362).

B. H. B.

**Analyses of Idocrase from Ala and Monzoni.** By E. LUDWIG and A. RENARD (*Jahrb. f. Min.*, 1884, 1, Ref., 24—25).—The results of the analyses are:—

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	H <sub>2</sub> O.	Total.
I ..	37·36	0·18	4·02	0·39	16·30	36·65	3·02	2·89	100·81
II ..	37·50	0·28	3·76	0·33	16·22	36·31	3·13	2·14	99·68

I. Grass-green idocrase (vesuvian) from Ala; sp. gr. 3·427.

II. Yellowish-brown idocrase from Monzoni; sp. gr. 3·413.

These analyses differ from previous analyses in giving no appreciable quantities of alkalis, and a very low percentage of FeO.

B. H. B.

**The Kersantite Vein of the Upper Harz.** By A. V. GRODDECK (*Jahrb. f. Min.*, 1884, 1, Ref., 68—70).—The author has discovered a vein of kersantite, 1 m. wide and 8 m. broad, traversing the Upper Devonian and Culm beds near Lauthenthal. He distinguishes three varieties of the rock: 1. Normal kersantite of a bluish-black colour, closely resembling that from Laveline in the Vosges. 2. A variety resembling quartz porphyry; and 3. A violet or reddish variety. Analyses of these three varieties are given (I, II, and III), as well as an analysis of kersantite from Laveline, (IV) made for the sake of comparison.

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.
I ...	54·80	0·30	11·20	3·42	0·05	4·80	0·40	8·32	6·00
II ...	62·00	0·20	10·96	5·54	0·05	4·41	0·41	1·02	6·52
III ...	50·80	0·10	7·93	4·62	0·05	4·67	0·41	10·00	4·75
IV ...	52·61	0·50	14·64	1·36	0·35	6·75	0·30	7·30	7·20

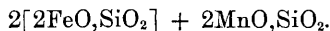
	H <sub>2</sub> O.	K <sub>2</sub> O.	Na <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	CO <sub>2</sub> .	Cu.	S.	Total.	Sp. gr.
I ...	2·82	1·25	1·15	0·40	4·63	—	—	99·54	2·72
II ...	2·99	2·46	1·78	0·35	0·44	—	—	99·13	2·60
III ...	2·02	0·95	0·99	0·40	12·70	—	—	100·39	2·68
IV ...	2·70	0·95	0·82	0·30	3·40	0·24	0·10	99·52	—

B. H. B.

**Manganese Minerals from Vester-Silfberg in Dalarne.** By M. WEIBULL (*Jahrb. f. Min.*, 1884, 1, Ref., 20—22).—1. *Ingelströmite*.—This mineral, described by Ingelström as knebelite, forms part of the gangue of the iron-manganese ores. It forms greyish-white crystalline masses with glassy lustre, splintery fracture and sp. gr. 4·17. The analysis gave:—

SiO <sub>2</sub> .	FeO.	MnO.	MgO.	CaCO <sub>3</sub> .	Total.
29·94	46·88	18·83	3·01	1·14	99·80

It is a member of the olivine-group with the composition,



2. *Alumina garnet containing manganese* occurs in grains. The analysis gave the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	Total.
36·03	20·91	21·26	17·79	4·43	100·42

3. *Silfbergite* occurs in translucent, honey-yellow columns with a glassy lustre and white streak. H. 5·5; sp. gr. 3·446. The mean of three analyses gave:—



SiO <sub>2</sub> .	FeO.	MnO.	MgO.	CaO.	Ignition.	Total.
48·83	30·49	8·34	8·39	1·74	0·44	98·23

From the analysis the formula  $4\text{FeO}, \text{SiO}_2 + 2\text{Mg}(\text{Ca})\text{O}, \text{SiO}_2 + \text{MnO}, \text{SiO}_2$  is deduced.

4. *Manganese-hedenbergite* has a greyish-green colour. H. 5; sp. gr. 3·55. The analysis gave:—

SiO <sub>2</sub> .	FeO.	MnO.	CaO.	MgO.	Alkalis.	Total.
48·29	24·01	6·47	17·69	2·83	0·22	99·51

which corresponds with the formula  $2(\text{FeO}, \text{SiO}_2 + \text{CaO}, \text{SiO}_2) + (\text{MnMg})\text{O}, \text{SiO}_2$ .

5. *Lime-diallogite*.—The mean of two analyses gave:—

CO <sub>2</sub> .	MnO.	FeO.	CaO.	Insol. residue.	Total.
40·58	24·60	6·95	26·71	1·15	99·99

By the action of the atmosphere this mineral is decomposed into *wad* with the following composition:—

CaO.	MnO.	FeO.	H <sub>2</sub> O.	Insol. residue.	Total.
4·38	61·56	20·51	8·43	3·23	98·11

B. H. B.

**Artificial Crystals of Manganese-iron-olivine.** By H. LASPEYRES (*Jahrb. f. Min.*, 1884, 1, Ref., 27—28).—At the steel works near Schwelm, crystals of manganese-iron-olivine were found on the sandstone bottom of a forge-hearth. The mean of two analyses gave the following results:—

Metallic Fe.	Sand.	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	SiO <sub>2</sub> .	Total.
0·67	16·02	0·77	44·00	13·83	25·21	100·50

After the removal of the metallic iron, the mechanically-mixed quartz sand and the Fe<sub>2</sub>O<sub>3</sub>, the analysis of the pure slag gave:—

SiO <sub>2</sub> .	FeO.	MnO.	Total.
30·36	52·98	16·66	100·00

representing the formula  $\text{MnFe}_2\text{Si}_2\text{O}_8$ .

The crystals have the well-known olivine form.  $\infty P\infty$ ,  $\infty P$ ,  $2P\infty$ .

B. H. B.

**Artificial Production of Spessartite or Manganese-garnet.** By A. GORGEU (*Compt. rend.*, 97, 1303—1305).—When 1 part of finely powdered pipe-clay and about 15 parts of nearly pure and dry manganese chloride are fused at a cherry-red heat in a current of hydrogen saturated with aqueous vapour by passing through a warm solution of potassium permanganate, a regulus is obtained which, when treated successively with water and dilute hydrochloric acid, yields a residue of yellowish crystals identical in composition, crystalline form (icositetrahedrons), and other properties, with spessartite, but slightly softer than the natural mineral (H. = 6—7; spessartite

above 7). By substituting calcium chloride for manganous chloride, the corresponding calcium compound is obtained. Melanite is the only variety of garnet which has hitherto been prepared artificially.

C. H. B.

**The Supposed Pre-Cambrian Rocks of St. David's.** By A. GEIKIE (*Journ. Geol. Soc.*, 1883, 261—325; *Jahrb. f. Min.*, 1884, 1, Ref., 88—91).—This paper was written to refute the views advanced by Dr. Hicks that there are, at St. David's, three distinct Pre-Cambrian formations: the "Dimetian," the "Arvonian," and the "Pebidian."

The Lower Cambrian beds at St. David's have been folded into an isoclinal curve, and the following rock groups may be recognised:—  
1. Volcanic group. 2. Quartz conglomerate. 3. Green and red shales and sandstones. 4. Purple and greenish grits, sandstones and shales.

The volcanic group consists mainly of tuffs with occasional breccias and bands of olivine-diabase. Analyses of the olivine-diabase from Rhosson (I), and from Clegyr Foig (II), are given—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.
I ....	45·92	18·16	1·18	9·27	0·19	7·19	10·07
II ....	45·38	16·62	4·06	8·63	0·14	8·19	9·41

	K <sub>2</sub> O.	Na <sub>2</sub> O.	Ignition.	Insoluble residue.	Total.	Sp. gr.
I ....	1·78	2·12	4·22	0·04	100·14	2·96
II ....	0·71	2·20	4·34	0·08	99·76	2·99

The tuffs are partly basic, derived from the disruption of diabase lavas, and partly acid from the destruction of fine felsites. A mass of granite has risen through the eastern limb of the isocline, and this granite is the "Dimetian" formation of Hicks. The metamorphism associated with the granite consists in the hardening of certain bands of rock which have been converted into flinty aggregates. These contact-products represent the "Arvonian" formation of Hicks.

B. H. B.

**Anorthitic Rock at Saint Clement, Puy de Dôme.** By F. GONNARD (*Compt. rend.*, 97, 1447—1449).—This rock consists essentially of anorthite and green pyroxene, and therefore belongs to the eukrite-group, but it is also characterised by containing, in unusual abundance, long silky fibres of wollastonite, sometimes almost colourless, but generally white, enclosing green grains of pyroxene, some rare crystals of reddish-brown sphene, and small, very brilliant, transparent or translucent crystals of brown vesuvianite. The wollastonite also forms small veins 2—3 mm. in thickness. The rock also contains quartz, though not in large quantity, and hornblende in deep green fibrous masses, black crystalline bundles, and short crystals. At the outcrop, the rock has weathered, and the constituent minerals have undergone considerable oxidation.

C. H. B.

**Presence of Phosphorus in Minette.** (*Dingl. polyt. J.*, **250**, 330.)—Specimens of this rock from Höhl, in Luxembourg, gave by analysis—

Fe <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	Mn <sub>2</sub> O <sub>4</sub> .	SiO <sub>2</sub> .
75·67	3·68	3·10	5·01	0·72	8·70

The phosphorus is in combination with the iron and not with the calcium. D. B.

**Glaucophane Schists of the Island of Groix.** By BARROIS (*Compt. rend.*, **97**, 1446—1447).—The island of Groix is formed mainly of alternating beds of mica schist and chloritic schists, but in some parts of the island there are found interstratified with these, beds which are characterised by the large number of minerals which they contain. The principal minerals are two varieties of amphibole distinct from hornblende, together with epidote, rutile, garnets, sphene, magnetite, chlorite and calcite in greater or less quantity. The predominant variety of amphibole is glaucophane in bluish polychroic crystals elongated along the faces *h'g'*. The prismatic faces are the dominant faces, and the crystals enclose rutile. The other variety is green amphibole, which is also highly polychroic, but in other directions. Epidote is very abundant in its usual forms, but does not show the common fan-like structure. The garnets are much cracked, as if they have been subjected to powerful mechanical action. The following is the probable order of consolidation: (1) rutile, sphene, magnetite, garnet; (2) glaucophane, epidote, white mica, quartz; (3) chlorite, green amphibole. C. H. B.

**The Crystalline Schists of Kaisersberg in Styria.** By H. v. FOULLON (*Jahrb. f. Min.*, 1884, **1**, Ref., 85—88).—This paper gives a petrographical description of the rocks of the Wurm Alp, near Kaisersberg, and of the Ennsthal and Paltenthal, all of which belong to the lower carboniferous period. Both in the older crystalline rocks, containing felspar, and in those of the carboniferous formation, the felspars are characterised by a remarkable richness in enclosures. In the rocks of the older crystalline formation, the felspar is mostly albite, but in the phyllite gneiss of the carboniferous formation mostly orthoclase, but partly microcline. Most of the crystalline rocks of the Paltenthal and Ennsthal are characterised by their great richness in titanium, which occurs sometimes as titaniferous iron, sometimes as rutile, or titanite. A number of rocks are remarkable for containing chloritoid, a mineral which up to the present time has not been frequently met with. It is here widely distributed, although the amount present in the rocks is often very small. Analysis of the chloritoid schist from the Wurm Alp gave the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	MgO.	CaO.	S.	H <sub>2</sub> O.	Organic matter.	Total.
78·84	8·26	6·48	trace	2·69	0·29	0·39	2·88	0·22	100·05

Those rocks of the Paltenthal and Ennsthal, which contain no

chloritoid, show a remarkable analogy to the rocks of the Wechsel mountains, recently described by A. Böhm. B. H. B.

**Elaeolite Syenite from Jivaara.** By F. J. WILK (*Jahrb. f. Min.*, 1884, 1, Ref., 75).—The Jivaara mountain is composed of elaeolite syenite. Near the summit a coarsely granular vein rock occurs, which is traversed by narrow veins of a finely granular variety. The coarsely granular vein rock is essentially a mixture of elaeolite and jivaarite (titaniferous lime-iron garnet), with subordinate pyroxene, almost entirely converted into amphibole. In contact with the altered pyroxene, cancrinite (sp. gr. 2.45) occurs, which encloses minute columns of pyroxene and amphibole, rich in soda. Felspar does not occur in this rock. In the finely granular variety, unaltered pyroxene occurs; jivaarite also occurs, but cancrinite has not been observed. In addition to these minerals, the rock contains yellow grains of apatite and brown crystals of titanite. B. H. B.

**The Cheviot Andesites.** By J. J. H. TEALL (*Jahrb. f. Min.*, 1884, 1, Ref., 71—73).—The Cheviot district is largely composed of porphyrites, and, in addition to these, masses of volcanic ash and breccia occur, together with a remarkable rock, to which the name *pitchstone-porphyrity* has been given. The most important result of the author's examination is that this pitchstone-porphyrity is exactly similar to many of the augite-andesites of Hungary, Transylvania, Servia, Santorin, and America. An analysis of a specimen of the Cheviot rock (sp. gr. 2.54) gave the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Loss.	Total.
63.0	14.9	4.7	4.8	2.8	4.0	1.9	4.0	100.1

The Cheviot porphyrites are, for the most part, only altered andesites. An analysis of a dark purple porphyrite (sp. gr. 2.56) from Shillmoor Farm gave:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Loss.	Total.
64.2	16.0	4.3	1.7	2.5	2.9	5.9	3.3	100.8

In conclusion, a specimen of Tuedian "porphyrite" from Stichill is described. The chemical analysis of the rock (sp. gr. 2.95) gave:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.
47.53	14.95	6.73	8.04	0.73	8.50
MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	Loss.	Total.
7.41	2.98	1.12	trace	1.95	99.94

It appears from microscopic and chemical examination that the rock is not a porphyrite, but a member of the basaltic family. B. H. B.

**The Biotite-holding Amphibole-granite from Syene.** By A. STELZNER (*Jahrb. f. Min.*, 1884, 1, Ref., 67—68).—This paper gives the results of the microscopic examination of sections of the rock of

the obelisk lately transported to New York from Alexandria. The rock was found to consist of microcline, oligoclase, quartz, hornblende, biotite, titanite, apatite, magnetite, and zircon. Viridite and pistazite are exceedingly rare. B. H. B.

**The Trachyte Region of the Rhodope.** By A. PELZ and E. HUSSAK (*Jahrb. f. Min.*, 1884, 1, Ref., 75).—An important microscopic examination of a number of younger eruptive rocks from the Rhodope showed a remarkable analogy to the rocks of the Transylvanian eruptive district. The specimens examined belong partly to the liparites and partly to the andesites. Among the latter, biotite-andesite, containing augite, predominates. Amphibole and augite andesites are of rarer occurrence. B. H. B.

**Analysis of the Rocky Portion of the Syssiderite of Atacama.** By S. MEUNIER (*Jahrb. f. Min.*, 1884, 1, Ref., 32).—The proportions in which the different minerals are present in the rocky portion of the syssiderite of Atacama may be thus expressed:—Magnesian pyroxene, 9·0 per cent.; schreibersite, 4·0 per cent.; chromite, 1·2 per cent.; anorthite, 0·1 per cent.; pyrrhotine, 0·5 per cent.; and olivine, 85·2 per cent. B. H. B.

**Basic Eruptive Rocks of Mâconnais and Beaujolais.** By A. MICHEL-LEVY (*Jahrb. f. Min.*, 1844, 1, Ref., 64—67).—The majority of the pre-granitic basic eruptive masses, which burst through the Cambrian slates and quartzites of Mâconnais and Beaujolais, are granular mixtures of titanite, magnetite, titaniferous iron, pyroxene, and labradorite, and should, according to the author, be classed as diabases. Of these, the author distinguishes two classes: granitoid diabases and ophitic diabases. The felspar of these rocks varies from oligoclase to anorthite; the pyroxene is very frequently converted into amphibole, and when the alteration is complete, rocks are formed, which the author calls diorites. In the series there are a certain number of rocks with a porphyritic structure and holo-crystalline microlithic ground-mass, or in other words, the rocks are developed as amphibolic porphyrites. The disseminated felspar is labradorite, and the microliths of the ground-mass consist of oligoclase. Varieties are exceptionally met with, in which the basicity is exaggerated and the felspar disappears, but olivine never occurs. B. H. B.

**Basalt from Naurod, near Wiesbaden.** By F. SANDBERGER (*Jahrb. f. Min.*, 1884, 1, Ref., 79—80).—The rock is, in general, a limburgite containing plagioclase and nepheline. The following are analyses:—I. Of the portion of the rock soluble in hydrochloric acid. II. Of the insoluble portion. III. Complete analysis of the rock:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.
I ..	18·67	11·89	2·33	5·61	0·08	2·65
II ..	26·57	7·33	2·88	—	—	6·53
III ..	45·24	19·22	5·21	5·61	0·08	9·18



MgO.	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	SiO <sub>2</sub> .	S.	P.	Total.
23·4261	0·8945	1·0884	0·2387	37·6257	2·5432	0·1532	99·9698

The author believes the metallic portion of the meteorite to have the composition of octibehite or teanite, whilst the non-metallic portion appears to consist of olivine and bronzite, both with excess of iron, and troilite.

C. E. G.

**Contribution to the Geological History of the Pallas Meteoric Iron.** By S. MEUNIER (*Jahrb. f. Min.*, 1884, 1, Ref., 31—32).—According to the author, the iron sulphide in many meteorites has originated from the action of sulphuretted hydrogen on grains of nickel iron, as may be clearly seen in the chondrite of Knyahinya, where the grains consist half of nickel iron and half of iron sulphide. In the meteorite of Krasnojarsk (Pallas iron), this is not the case; here the iron sulphide was formed first, and the nickel iron therefore could not have originated at a very high temperature. The author supposes that fissures with fragments of olivine crystals originally existed; then iron sulphide was probably formed by the action of sulphuretted hydrogen on iron and nickel chlorides, and lastly the various compounds of nickel and iron were concentrically deposited. The Pallas iron is an example of vein formation, analogous to the oldest terrestrial metalliferous deposits, and the mode of formation especially resembles that of tin ore veins. The Pallas iron, therefore, should not be classed with the other pallasites of G. Rose.

B. H. B.

**The Cranbourne Meteorite.** By W. FLIGHT (*Jahrb. f. Min.*, 1884, 1, Ref., 33—35).—Two masses of meteoric iron were discovered at Cranbourne, near Melbourne, in 1854. The Bruce meteorite, the larger mass, is now in the British Museum. The meteorite consists entirely of metallic minerals, and contains no rocky matter whatever. The absence of combined carbon was established by decomposing the iron in a solution of sodium chloride by a galvanic current. The iron thus dissolved was found to have the composition given under I, while the analyses II—VI give the constituents, other than iron, in some of the largest nickel-iron crystals and cleavage plates of various thicknesses:—

	I.	II.	III.		IV.		V.	VI.
Residue.....	0·93	1·40	0·07		0·10	0·11	—	—
Ni.....	7·65	8·06	7·71	7·53	9·76	6·48	9·80	9·05
Co.....	0·50		0·60		0·76		—	—
Cu.....	0·02	—	—		—		—	—
Si.....	0·17	—	—		—		0·06	—
P.....	—	—	0·19		0·02		—	—

In addition to nickel-iron a number of other constituents have been identified and analysed, for example, the thin paper-like plates which lie between the large plates of the nickel iron crystals. They contain 70·14 per cent. Fe and 29·74 per cent. Ni. This is evidently an alloy of well-defined composition, and is the constituent of nickel iron

which forms the fine lines constituting the Wiedemannstädtian figures. It is probably identical with the *tänite* of G. Rose or the meteorine of Zimmermann. The author proposes to call it *Edmondsonite*. The insoluble residue mentioned above, which forms nearly 1 per cent. of the mass, consists of strongly magnetic prisms apparently identical with the *Rhabdite* of Rose. The mean of three analyses gave—

Fe.	Ni.	P.	Total.
49.33	38.24	12.95	100.52

which corresponds with the formula  $(\text{Fe}_4\text{Ni}_3)\text{P}$ .

The coarse insoluble powder is very brittle and magnetic, and dissolves easily in nitric acid.

The mean of two analyses gave :—

Fe.	Ni.	P.	Total.
56.12	29.18	13.50	98.80

This is doubtless the mineral *schreibersite*  $(\text{Fe}_2\text{Ni})_7\text{P}$ . A large brass-coloured crystal of this substance gave on analysis :—

Fe.	Ni.	P.	Total.
69.55	(14.41)	16.04	100.00

A curious crystal was met with on one or two occasions. It consisted of a square prism with bright and metallic sides, and a square centre of a dull black colour. The analysis corresponded with the formula  $(\text{Fe}_7\text{Ni}_2)_8\text{P}$ . Graphite occurs in sheet-like masses or nodules, sometimes enclosing troilite. The troilite is not magnetic, and is sometimes accompanied by daubreelite. When digested with carbon bisulphide 0.0207 per cent. sulphur was dissolved. The nickel-iron was further examined for occluded gases, and was found to contain 3.59 times its volume of gas having the following composition :—

$\text{CO}_2$ .	CO.	H.	$\text{CH}_4$ .	N.	Total.
0.12	31.88	45.79	4.55	17.66	100.00

B. H. B.

**Geological History of the Syssiderite of Lodran.** By S. MEUNIER (*Jahrb. f. Min.*, 1884, 1, Ref., 32).—The author regards the meteorite of Lodran as a sandstone with metallic cementing material, analogous to the ores of Commern, in Rhine Prussia, and of Coro-Coro, in Bolivia. The meteoric sand may be imagined to have been produced by volcanic action, and the metallic cement by the reduction of chlorides by means of hydrogen.

B. H. B.

**The Meteorite of Sewrjukowo.** By A. EBERHARD (*Jahrb. f. Min.*, 1884, 1, Ref., 30—31).—This meteorite fell on May 12th, 1874, at Sewrjukowo. Its weight was 98 kilos. The following constituents were discovered: nickel-iron phosphide; olivine; bronzite; enstatite; and troilite. Analysis I gave the composition of the silicates soluble in aqua regia; II that of the insoluble residue; III and IV gave the composition of the chromite and nickel-iron phosphide :—



	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.
I ..	43·60	1·10	14·90	1·20	36·70
II ..	54·09	5·25	10·12	3·90	22·27
III ..	—	28·50	31·50	—	—
	K <sub>2</sub> O.	Na <sub>2</sub> O.	Cr <sub>2</sub> O <sub>3</sub> .	Chromite.	Total.
I ..	1·10	2·40	—	—	101·0
II ..	0·54	1·69	1·13	1·01	100·0
III ..	—	—	39·40	—	99·4
	Fe.	Ni.	Co.	P.	Total.
IV ..	87·6	11·4	0·6	0·4	100·0

The author calculates that the meteorite is composed of 0·94 per cent. troilite; 4·13 per cent. magnetic pyrites; 15·94 per cent. nickel-iron phosphide; 47·74 per cent. silicates decomposed by acids, probably olivine mixed with some other silicate; and 31·25 per cent. silicates not decomposed by acids.

B. H. B.

## Organic Chemistry.

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### Action of Sodium Ethoxide on Bromethylidene Bromide.

By A. MICHAEL (*Amer. Chem. J.*, **5**, 192—197).—Tawildarow has stated (this Journal, 1874, 348) that two dibromethylenes are formed by the action of sodium ethoxide on bromethylidene bromide; one boiling at 91°, the other at 157°. A third dibromethylene boiling at 109° has been obtained by Sabanejeff by the reduction of acetylene tetrabromide, or by the direct addition of bromine to acetylene. As the existence of three dibromethylenes would necessitate the assumption of the presence of a dyad carbon-atom in one of the isomerides, the author has repeated Tawildarow's experiments, but fails to obtain the dibromethylene boiling at 157°, the products of the reaction being bromacetylene and  $\alpha$ -dibromethylene (boiling at 86—88°). The remainder of the paper is occupied with a discussion of the proofs advanced by Demole (*Abstr.*, 1881, 142) of the correctness of the formula assigned by him to  $\alpha$ -dibromethylene. A. J. G.

**Formation of Acetylene from Iodoform.** By P. CAZENEUVE (*Compt. rend.*, **97**, 1371—1373).—Iodoform in contact with finely-divided silver is rapidly converted into acetylene even in the cold,  $2\text{CHI}_3 + 3\text{Ag}_2 = 6\text{AgI} + \text{C}_2\text{H}_2$ . The silver is more active if mixed with finely-divided copper. Many other metals, such as mercury, zinc, and iron, also decompose iodoform in presence of water, forming a metallic iodide and liberating acetylene.

When iodoform is mixed with equal weights of powdered zinc and water, gas is given off spontaneously; or if gently heated a liquid heavier than water is also formed having an agreeable ethereal

odour, and a sweet taste; it is in all probability an iodo-derivative. The gas which is evolved is a mixture of acetylene and an iodo-derivative which burns with a pale blue flame with purplish edges, forming hydriodic acid and depositing free iodine.

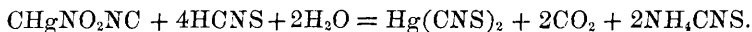
If a saturated solution of copper sulphate is used instead of water, the evolution of gas is still more rapid, for the zinc-copper couple which is produced not only decomposes the iodoform more rapidly, but also partially decomposes the iodo-derivatives. (*Comp. Gladstone and Tribe, this Journal, 1875, 512.*) The action of a moist zinc-copper couple on iodoform may be shown as a lecture experiment.

This reaction confirms the accepted constitution of acetylene, and is analogous to the action of zinc on methyl iodide. Probably the action of zinc on di-iodo-methane would give rise to ethylene.

Acetylene is also formed when iodoform is decomposed by heat.

C. H. B.

**Experiments on Mercury Fulminate.** By A. EHRENBURG (*J. pr. Chem.* [2], 28, 56—57).—Aqueous thiocyanic acid does not act on mercury fulminate in the same manner as hydrochloric acid, which forms hydroxylamine hydrochloride, but according to the equation—



Ammonium and potassium thiocyanates decompose the fulminate in a manner similar to the alkaline chlorides.

Mercury fulminate heated with ethyl sulphide or with carbon bisulphide in presence of alcohol and water, yields mercury sulphide and fulminurates: if water is excluded from the reaction, other products are formed, and the ammonium fulminate is therefore merely a secondary product. Further experiments are being made.

H. B.

**Action of Carbon Oxychloride on Ethylene Glycol.** By J. NEMIROWSKY (*J. pr. Chem.* [2], 28, 439—440).—By the action of 1 mol. pure glycol on 1 mol. carbon oxychloride in a closed tube at the ordinary temperature, the author has obtained glycol-carbonate,  $\text{CO}(\text{OCH}_2)_2$ , with evolution of hydrochloric acid. This substance is stable, soluble in water, alcohol, and in warm ether, from which on cooling it crystallises in colourless needles. The author continues his investigation.

A. B.

**Action of Carbonic Anhydride on Calcareous Solutions of Sugar.** By D. LOISEAU (*Compt. rend.*, 97, 1139—1141).—A 10 per cent. solution of sugar is saturated with calcium hydroxide at 20—25°, filtered, and treated with a current of carbonic anhydride. A relatively considerable quantity of the gas is absorbed, and if the liquid is agitated continually, it does not change in appearance; but if the liquid is allowed to remain at rest so that an excess of the gas acts on the same liquid surfaces, a gelatinous white precipitate is produced, which at first redissolves easily in the sugar solution. If portions of the liquid are removed from time to time, it is found that as the passage of the gas is continued up to a certain point, the solu-

tion loses its power of yielding a precipitate of tribasic calcium succrate when heated, or of bibasic calcium succrate when cooled. It would appear that the presence of the calcium carbonate prevents the precipitation of the succrates, whilst the presence of the latter prevents the precipitation of the carbonate. If the passage of the carbonic anhydride is continued still further, the solution still fails to yield a precipitate of bibasic calcium succrate when cooled to  $0^{\circ}$ , but acquires the property of yielding a precipitate when heated. This contains calcium carbonate, calcium hydroxide, and sugar, and redissolves in the mother-liquor on cooling, like the tribasic succrate.

If the passage of the gas is continued until the liquid becomes slightly turbid and is then stopped, an abundant gelatinous precipitate separates; this contains sugar, calcium hydroxide, and calcium carbonate, and when it is mixed with about an equal volume of the calcareous sugar solution which has not been treated with carbonic anhydride, the precipitate dissolves as a whole.

C. H. B.

**Action of Acetic Anhydride and Acetic Chloride on Maize and Potato-starch.** By A. MICHAEL (*Amer. Chem. J.*, 5, 359—360).—The acetyl derivatives obtained by heating these starches with acetic anhydride are not coloured by iodine; the granules under the microscope could not be distinguished from those of the parent starches. 2 grams of maize starch was heated with 5 grams of acetic chloride for 15 hours at  $55$ – $58^{\circ}$ ; the product was extracted with chloroform, the solution evaporated to dryness, and the residue dissolved in hot alcohol and treated with bone-black. On cooling, a greyish-white substance separated, from which, by again dissolving in hot alcohol and cooling, a white amorphous substance was obtained. This softened at  $148^{\circ}$ , and melted constantly at  $151$ – $152^{\circ}$ . On adding water to the first alcoholic filtrate, it gave a substance melting at  $128$ – $129^{\circ}$ . Very similar results were obtained with potato-starch.

A. J. G.

**Hydration of Crotonaldehyde.** By A. WURTZ (*Compt. rend.*, 97, 1169—1172).—Carefully purified crotonaldehyde is mixed at  $0^{\circ}$  with twice its weight of water and the same amount of hydrochloric acid, and the mixture is left at rest exposed to light for several hours. After some time, it becomes brown and the odour of crotonaldehyde almost disappears. The liquid is neutralised with sodium carbonate in order to precipitate resins, and the filtrate is agitated with ether. On evaporating the ether and fractionating the residue, aldol, paralldol, and other condensation products, and dialdane are obtained, but the yield of the first substance is only small. Possibly the crotonaldehyde at first combines with hydrochloric acid, and the compound thus formed reacts with the water, thus:  $\text{CHMeCl} \cdot \text{CH}_2\text{CHO} + \text{H}_2\text{O} = \text{CHMe}(\text{OH}) \cdot \text{CH}_2\text{CHO} + \text{HCl}$ . Crotonaldol could not be isolated.

C. H. B.

**Formation of Crotonaldehyde and  $\beta$ -Hydroxybutyraldehydes from Acetaldehyde.** By A. MICHAEL and A. KOPP (*Amer. Chem. J.*, 5, 182—191).—The authors' experiments show conclusively that  $\beta$ -hydroxybutyric aldehyde (aldol) is the primary product of the

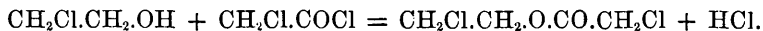
action of zinc chloride on acetaldehyde, the formation of crotonaldehyde being due to the decomposition by heat of the aldol first formed. Potassium and sodium salts of neutral reaction are without action on acetaldehyde. Saturated solutions of potassium salts of alkaline reaction and dilute solutions of sodium and potassium hydroxides behave like zinc chloride, whilst sodium salts of alkaline reaction give crotonaldehyde, oily substances, and probably aldol in small quantity. Dry potassium carbonate converts acetaldehyde into aldol, whilst dry sodium carbonate has no action on it. Aldol, when heated with moderately concentrated solutions of alkaline salts or of zinc chloride, is converted partly into crotonaldehyde, partly into liquids of higher boiling point, which yield crotonaldehyde on distillation.

A. J. G.

**Convenient Method for Preparing Bromacetic Acid.** By A. MICHAEL (*Amer. Chem. J.*, 5, 202—203).—This method is based on the formation and decomposition at 100° of the compound  $(C_2H_4O_2, Br_2)_4.HBr$ . A mixture of glacial acetic acid and bromine (the latter slightly in excess of the theoretical quantity) with a small quantity of carbon bisulphide, is heated at 100° in a flask provided with a reflux condenser until hydrobromic acid ceases to be evolved; the product is then submitted to fractional distillation. The yield is about 90 per cent. of the theoretical quantity.

A. J. G.

**Monochlorethyl Monochloracetate.** By L. HENRY (*Compt. rend.*, 97, 1308—1311).—Monochlorethyl monochloracetate is easily obtained by the action of monochloracetic chloride on ethylene monochlorhydrin,



This reaction illustrates the difference between the action of the primary alcoholic chain  $CH_2.OH$  on the two chains  $CH_2Cl$  and  $COCl$ . Monochlorethyl monochloracetate is a colourless limpid liquid, with a slightly pungent odour and a burning taste, insoluble in water, and not affected by the action of light. It boils at 197—198° (uncorr.); sp. gr. at 10·6° = 1·3217.

When monochlorethyl monochloracetate is gently heated with an alcoholic solution of sodium iodide, sodium chloride is precipitated, and monochlorethyl moniodo-acetate,  $CH_2Cl.CH_2.O.CO.CH_2I$ , is formed. It is a colourless oily liquid, insoluble in water; sp. gr. at 18° = 1·9540. It becomes brown when exposed to light, and cannot be distilled without decomposition. Its vapours are very irritating to the eyes. When heated with water for some time, the monochlorethyl moniodo-acetate is completely decomposed, but the liberated iodoacetic acid is very unstable, and splits up immediately.

Monochlorethyl monobromacetate is obtained by treating the preceding compound with bromine and removing the excess of the latter by means of hydrogen potassium sulphite. It is a colourless somewhat viscous liquid, insoluble in water, with a burning taste, and a faint odour exciting tears. It boils at 213—215° (uncorr.) with slight decomposition; sp. gr. at 11·4° = 1·6499. When heated for

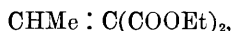
some time with several times its own volume of water, monochlor-ethyl monobromacetate is completely decomposed, and yields glycol monochlorhydrin and monobromacetic acid.

It is evident that in presence of monochlorethyl monochloracetate, sodium iodide exhibits an exclusive preference for the chain  $\text{CH}_2\text{Cl}$  united with the group  $\text{CO}$  in the acetic part of the molecule. This reaction affords further evidence of the influence exerted by oxygen on chlorine united with a carbon-atom which is directly connected with the carbon-atom to which the oxygen is attached.

C. H. B.

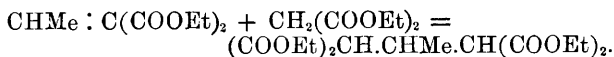
**Action of Fatty Aldehydes on Malonic Acid and its Ethyl Salt.** By T. KOMMENOS (*Annalen*, **218**, 145—169).—From the general nature of the reaction obtaining between benzaldehyde and ethyl malonate, it would *a priori* be expected that fatty aldehydes would form the ethyl salt of a dicarboxylic acid of general formula,  $\text{CHR}.\text{C}(\text{COOH})_2$ , readily decomposing into carbonic anhydride and an aldehyde-substituted acetic acid,  $\text{CHR} : \text{CH}.\text{COOH}$ .

Former researches of Crismer have established that aldehyde forms two condensation-products with ethyl malonate, one



and the other,  $(\text{COOEt})_2\text{CH}.\text{CHMe}.\text{CH}(\text{COOEt})_2$ . In the present research, it is shown that aldehyde and malonic acid yield, besides crotonic acid, ethylidene-diacetic acid,  $\text{CHMe}(\text{CH}_2.\text{COOH})_2$ . In the course of the study of the reaction between aldehyde or paraldehyde and malonic acid when heated with acetic acid or its anhydride, there was noticed the formation of a small quantity of an oil boiling between  $282$ — $284^\circ$ , which solidified on cooling in the form of prismatic crystals of composition  $\text{C}_6\text{H}_2\text{O}_3$ , although the principal product of the reaction was crotonic acid. The former compound is soluble in alcohol and ether. It dissolves in hot water as an anhydride of an acid to form a dibasic acid,  $\text{C}_6\text{H}_{20}\text{O}_4$ , or *ethylidene-diacetic acid*,  $\text{CHMe}(\text{CH}_2.\text{COOH})_2$ , which crystallises in small prisms or thick tables, melting at  $85^\circ$ , soluble in water, alcohol, and ether, sparingly soluble in benzene and chloroform. By distillation it is readily decomposed into water and the anhydride. Its lead and calcium salts are crystalline substances.

By the action of aldehyde on ethyl malonate there is formed, besides ethyl ethylidene-malonate,  $\text{CHMe} : \text{C}(\text{COOEt})_2$ , the *ethyl salt of ethylidenedimalonic acid*,  $\text{CHMe}[\text{CH}(\text{COOEt})_2]_2$  (*vide supra*); but the yield of the latter compound is always small. It is a golden coloured liquid, boiling at  $209^\circ$  under a pressure of 20 mm. As it may also be obtained by heating ethylidene malonate with ethyl malonate, it would appear probable that its formation from ethyl malonate and aldehyde is due to the combination of unaltered ethyl malonate with ethyl ethylidene-malonate, thus :

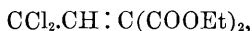


When the ethyl salts of ethylidene malonate and ethylidene dima-

lonate are saponified with alcoholic potash, they yield ethylenediacetic acid.

*Propylidene-acetic acid*,  $\text{CHEt} : \text{CH}.\text{COOH}$ , and *propylidene-diacetic acid*,  $\text{CHEt}(\text{CH}_2.\text{COOH})_2$ , are obtained simultaneously by the action of propaldehyde on malonic acid in the presence of acetic acid. The former is a colourless liquid, resembling crotonic acid in its smell; it boils between  $194^\circ$  and  $198^\circ$ ; sp. gr. = 0.9922. Its silver salt is a white, voluminous, sparingly soluble precipitate. The latter, or  $\beta$ -ethylglutamic acid, crystallises in white prisms which melt at  $66^\circ$ , easily soluble in water and alcohol.

Chloral and ethyl malonate react in like manner to form a condensation-product, *ethyl trichlorethylidene-malonate*,



a colourless viscid liquid boiling at  $160$ — $164^\circ$  under a reduced pressure of 23 mm. V. H. V.

**Isopropylsuccinic or Pimelic Acid.** By W. ROSER (*Annalen*, **220**, 271—278).—By acting on sodium malonic ether with ethyl  $\alpha$ -bromoisovalerate, the author obtained the ether



a clear liquid which distils at  $276$ — $278^\circ$ , and has an unpleasant and bitter taste. The free acid obtained by the saponification of the ether with potash, is easily soluble in alcohol, ether, and water, and yields monoclinic needles. It melts at  $160^\circ$ , evolving carbonic anhydride at the same time. The *barium*, *silver*, *lead*, and *iron salts* are very sparingly soluble in water. When heated above its melting point, this acid gives off carbonic anhydride, and yields *isopropylsuccinic acid*. The latter acid is easily soluble in alcohol, ether, and water. It melts at  $114^\circ$ , and gives up water at a higher temperature, yielding its anhydride, which boils at  $245$ — $250^\circ$ . Its *calcium*, *silver*, *lead*, *copper*, and *iron salts* are sparingly soluble in water. These properties agree with those of pimelic acid obtained by Hlasiwetz and Grabowsky from camphoric acid. The identity of the two acids is further proved by the equal solubility of their calcium salts. Ammonium isopropylsuccinate, heated in a stream of ammonia, yields *isopropylsuccinimide*,  $\text{C}_7\text{H}_{11}\text{NO}_2$ . This imide is easily soluble in alcohol, ether, and light petroleum, more sparingly in water, and crystallises in small needles or tables. It melts at  $60^\circ$ , and distils undecomposed. L. T. T.

**Gluconic Acids from different Sources.** By A. HERZFELD (*Annalen*, **220**, 335—365).—The author has repeated the researches of Barth and Hlasiwetz, Habermann, Fudakowsky, Hönig, Kiliani, and Grieshammer on the acids obtained by the oxidation of the various carbohydrates. He finds that all the different *gluconic* and *dextronic acids* obtained by these investigators are in reality identical, the varying properties observed being due to the presence of saccharic acid as an impurity. The result is the same, whether the primary action on the carbohydrate be carried out with chlorine or bromine, and whether the halogen compound be decomposed by silver oxide or

the oxide of any other metal (lead, &c.), or by carbonates (basic zinc carbonate, &c.). When bromine is used, saccharic acid always accompanies the gluconic acid formed, the quantity being largest when zinc carbonate is used to decompose the halogen compound.

*Gluconic acid* forms a syrup, is monobasic, and does not reduce Fehling's solution. Its rotatory power for polarised light is  $[\alpha]_D = 4.8^\circ$ .

*Calcium gluconate*,  $(C_6H_{11}O_7)_2Ca + H_2O$ , crystallises in microscopic needles. *Barium gluconate*,  $(C_6H_{11}O_7)_2Ba + 3H_2O$ , crystallises in rhombohedral scales which are double refracting, and appear to belong to the triclinic system. On long standing over calcium chloride these crystals lose 2 mols.  $H_2O$ . A concentrated solution of the barium salt treated with a large excess of barium hydroxide gave a flocculent precipitate having the constitution  $C_6H_{12}O_8Ba$ .

Contrary to the statements of Wachtel, the author was unable to obtain mannitol by the reduction of gluconic acid. Attempts to prove the number of hydroxyl-groups in the acid by converting it into the acetyl compound were equally unsuccessful. The author believes the formula to be most probably  $OH.CH_2(CH.OH)_4COOH$ .

L. T. T.

**Antimony Derivatives of Mucic and Saccharic Acids.** By D. KLEIN (*Compt. rend.*, **97**, 1437—1439).—Antimonious oxide dissolves in a boiling solution of sodium hydrogen mucate, and on evaporation the clear liquid deposits a slightly gelatinous amorphous salt, which is very slightly soluble in cold, but is soluble in hot water. It is purified by solution in hot water, from which it separates on cooling. When dried at  $100^\circ$ , it forms a white porous mass of sodium muco-antimonite,  $C_4H_4(OH)_3(SbO)(COONa).COOH$ , analogous to ordinary tartar emetic. At  $145^\circ$  it loses  $H_2O$ , and at  $185^\circ$  it loses an additional  $\frac{1}{2}H_2O$ . The residue dissolves in warm water, reproducing the original salt. Above  $185^\circ$  it turns brown and decomposes. The potassium salt is precisely similar in appearance and composition, and can be obtained in the same way.

Ammonium hydrogen mucate solution dissolves antimonious anhydride, and if the solution is gently heated at about  $50^\circ$  it deposits a pulverulent salt on cooling; but if it is boiled, the resulting solution filters slowly, and has all the properties of colloids, and when concentrated and cooled, it gelatinises. Solutions of sodium hydrogen mucate and potassium hydrogen mucate yield similar products when boiled with antimonious anhydride. These antimony derivatives have no appreciable rotatory power. When a solution of ferric chloride is added in excess to a solution of normal ammonium mucate, a precipitate is produced; this dissolves in ammonia, forming a highly coloured solution which gelatinises after some days.

Mucic acid is much more soluble in a boiling solution of boric acid than in water, but no compound could be obtained similar to that formed by tartaric acid, and the solution has no rotatory power.

The acid saccharates also dissolve antimonious and antimony anhydrides. Potassium saccharate appears to form non-crystallisable derivatives with both these oxides.

C. H. B.



**Action of Methyl Iodide on Leucine and Analogous Compounds.** By G. KOERNER and A. MENOZZI (*Gazzetta*, **13**, 351—358).—The authors find that the first product of the action of methyl iodide on amidated acids dissolved in potash is generally “the iodide of a trimethylated acid which is at the same time a potassium salt;” in some cases this splits up in the course of the reaction, giving trimethylamine and the potassium salt of a new acid. The results obtained with leucine are described in this paper, but the authors also state that glycocine gives the potassium salt of iodide of trimethylglycocine, and that  $\alpha$ -alanine behaves in a similar manner. With  $\beta$ -alanine on the contrary the iodide splits up during the reaction, yielding trimethylamine (which forms trimethylammonium iodide with the excess of methyl iodide) and the potassium salt of a non-azotised acid, behaving in this respect like asparagine and aspartic acid.

When natural leucine obtained from casein is treated with methyl iodide and potassium hydroxide, the mixture becomes warm, and a slightly coloured neutral liquid is ultimately obtained. This is evaporated to dryness and extracted with absolute alcohol, which dissolves the potassium salt along with a small quantity of potassium iodide. After two or three crystallisations from alcohol, the salt  $C_6H_{10}(NMe_3I)COOK$  is obtained in very slender needles which are hygroscopic and very soluble in water. When the aqueous solution of this salt is treated with a solution of iodine in hydriodic acid, a heavy oil is precipitated which after a time solidifies to a mass of metallic green crystals of periodide of trimethyl-leucine. The *iodide of valero-betaïne*,  $C_9H_{20}NO_2I$ , may be obtained from this by suspending it in water, passing hydrogen sulphide in excess, filtering from sulphur, evaporating, and crystallising the residue from alcohol. The betaïne forms stellate groups of prisms, very soluble in water, but only sparingly in cold alcohol. It melts at  $191^\circ$  with decomposition, evolving trimethylamine. The iodide can be converted into the *chloride* by treatment with silver chloride. The *aurochloride*,



is deep yellow, and very sparingly soluble in water. It melts at  $163^\circ$ . The *platinochloride*,  $(C_6H_{11}O_2.NMe_3Cl)_2.PtCl_4$ , is orange-yellow and sparingly soluble.

If the potassium salt of the iodide of trimethyl-leucine is treated with silver hydroxide in slight excess, silver iodide is precipitated, and a strongly alkaline solution is obtained which has a feeble odour of trimethylamine. On distilling it, and heating the residue at  $120$ — $130^\circ$ , large quantities of trimethylamine are given off, and a residue is left; when this is acidulated with sulphuric acid and distilled in a current of steam, oily drops pass over, having a strongly acid reaction. This acid has the formula  $C_6H_{10}O_2$ , and decomposes carbonates readily. It resembles hydrosorbic acid in many points, but does not seem to be identical with it. It boils at  $124$ — $127^\circ$  under a pressure of 26 mm. The barium, calcium, zinc, and silver salts were prepared; the most characteristic salt is that of cadmium, which crystallises in long prisms united in stellate groups. The acid unites with hydrobromic acid, but the author has not yet examined the

product. Trimethylamine, and the acid just described, are not, however, the only products of this reaction, as the liquid left in the retort, after the steam distillation, yields a small quantity of a non-volatile acid when treated with ether; on examination this was found to be leucic acid.

When synthetical leucine obtained from isovaleraldehyde is treated with methyl iodide and potassium hydroxide in the manner above described, it yields the potassium salt of the corresponding iodide, from which the betaine and its salts may be prepared. When the base from synthetical leucine is decomposed by heat, it yields trimethylamine and two acids, one volatile,  $C_6H_{10}O_2$ , and the other a non-volatile hydroxy-acid,  $C_6H_{12}O_3$ . It is interesting to note that the volatile acid, which must have the constitution  $CHMe_2.CH:CH.COOH$ , is not pyroterebic acid, which confirms the opinion recently expressed by Fittig. The author will shortly describe these products more fully, and also those obtained from the leucine from normal valeraldehyde.

C. E. G.

**New Synthesis of Allantoin.** By A. MICHAEL (*Amer. Chem. J.*, **5**, 198—202).—Allantoin is obtained by heating equal weights of mesoxalic acid and carbamide at  $110^\circ$ . The remainder of the paper consists of speculations on the constitution of uric acid.

A. J. G.

**Fluobenzene and Fluotoluene.** By E. PATERNÒ and V. OLIVERI (*Gazzetta*, **13**, 533—535).—Fluobenzene,  $C_6H_5F$ , is prepared by heating in sealed tubes with strong hydrochloric acid the potassium salt of fluobenzenesulphonic acid, which is formed from sulphanilic acid through the medium of the diazo-compound (Lenz, *Ber.*, **10**, 1135, and **12**, 580). Fluobenzene is a limpid liquid, smelling like benzene, boiling at  $85-86^\circ$ , and not solidifying at  $-20^\circ$ . Vapour-density, exp. 3.13; calc. 3.36 [ $H = 1$ ].\*

*Fluotoluene*,  $C_7H_7F$ , is obtained in like manner by converting *p*-amidotoluenesulphonic acid into the diazo-compound and decomposing this with hydrofluoric acid. It is a liquid having a very decided odour of bitter almonds, and boiling at  $114^\circ$ .

H. W.

**Cymene from Homocumic Acid.** By E. PATERNÒ (*Gazzetta*, **13**, 535—537).—Cumic compounds contain isopropyl, and cymene contains normal propyl; nevertheless, in the transformations of these bodies, the cumic compounds invariably yield cymene, and cymene on the other hand is converted into cumic compounds. The experiments of Nencki and Ziegler, and those of Jacobsen, have shown that cymene, by oxidation in the animal organism, is converted into cumic acid, and from the recent investigations of Errera (*Gazzetta*, **13**, 421, and p. 300 of this volume), it appears that the action of chlorine on

\* The supposed fluobenzene which Schmidt and Gehren obtained (*J. pr. Chem.* [2], **1**, 400), by distilling calcium fluobenzoate with lime was nothing but phenol, agreeing with that compound in composition, boiling point, and vapour-density; no attempt was made by Schmidt and Gehren to determine the fluorine supposed to be present. Paternò and Oliveri, in repeating the experiment, obtained a considerable quantity of pure phenol; and after treating the product with potash, they obtained a liquid boiling above  $240^\circ$ , and probably consisting for the most part of diphenyl oxide.

boiling cymene gives rise to cumyl chloride,  $C_{10}H_{13}Cl$ , identical with that which is obtained from cumyl alcohol,  $C_{10}H_{14}O$ . On the other hand, Kraut (*Annalen*, 192, 224), by heating cumyl alcohol with zinc-dust, obtained cymene identical with that from camphor, and with that which Paternò and Spica prepared by reducing cumyl chloride with nascent hydrogen. Granting therefore that cymene contains normal propyl, and that the cumic compounds contain isopropyl, it follows that in the reactions just cited,  $Pr^{\alpha}$  is converted with the greatest facility into  $Pr^{\beta}$ . To throw further light upon this question, the author endeavoured to prepare isocymene or isopropyl-

methylbenzene,  $C_6H_4MePr^{\beta} = Me \langle \text{hexagon} \rangle CHMe_2$ , by the distillation

of homocumic acid,  $C_6H_4Me(C_3H_7).COOH$ . With this view, the calcium salt of homocumic acid was distilled with lime, whereby a hydrocarbon boiling at  $173-175^{\circ}$  was obtained, convertible into a sulphonic acid the barium salt of which dried at  $100^{\circ}$  had the composition  $(C_{10}H_{13}SO_3)_2Ba, 3H_2O$ . This shows that the cymene obtained from homocumic acid is not *p*-methylisopropylbenzene, but ordinary cymene, *i.e.*, *p*-methylpropylbenzene: for it is known that isocymene yields a sulphonic acid the barium salt of which crystallises, according to Jacobsen, with only 1 mol.  $H_2O$ .

This constancy of the transformation of cumic compounds into ordinary cymene, and the reverse, seems to indicate the identity of the radicle  $C_3H_7$  contained in the two classes of compounds; but the synthesis of propyl- and isopropyl-benzene, and the isomerism of cumic and normal propylbenzoic acids, are facts too well established to render such a view admissible.

H. W.

**Metabenzyl-toluene, Metatolyl Phenyl Ketone, Metabenzoyl-benzoic Acid, and their Reduction Products.** By P. SENFF (*Annalen*, 220, 225—253).—Metabenzyltoluene was obtained by the action of aluminium chloride on a mixture of xylyl chloride and benzene. The best yield is obtained when xylyl chloride is mixed with about 6—8 times its weight of benzene, about 1—2 per cent. of aluminium chloride added, and the whole gently heated on the water-bath. Before distillation the resulting liquid must be washed with water to free it from intermediate aluminium compounds. The fraction passing over between  $260-280^{\circ}$  was digested for five hours with sodium to free it from traces of an oxygenated compound from which it could not be separated by fractionating. *Metabenzyltoluene* is a colourless liquid, of slightly aromatic odour, and becomes viscid at low temperatures. It boils at  $275^{\circ}$  (col. in vapour) at 747 mm. pressure, and has sp. gr. 0.997 at  $17.5^{\circ}$ . It is easily soluble in alcohol, ether, benzene, chloroform, and glacial acetic acid. From the high-boiling bye-products the author isolated *disylylbenzene*, a yellowish oil boiling at  $392-396^{\circ}$ , and soluble in alcohol, ether, and glacial acetic acid; and also a body boiling between  $210-220^{\circ}$ , which he believes to be *dimethylantracene*, but has not obtained it quite pure. *Dinitrometabenzyltoluene* was prepared by the action of a large excess of nitric acid (sp. gr. 1.4) at  $90^{\circ}$ . It melts at  $141^{\circ}$ , is

soluble in boiling alcohol, benzene, and glacial acetic acid, and crystallises in long needles. *Dinitrometatolyl phenyl ketone* was prepared by the oxidation of the dinitro-body in acetic solution by means of chromic acid. It melts at  $145^{\circ}$ , and is easily soluble in benzene, chloroform, boiling acetic acid, and alcohol, and crystallises in needles or short prisms.

*Metabenzoylbenzoic acid*,  $C_6H_4\overline{Bz}.COOH$ , was obtained by the oxidation of the hydrocarbon by means of chromic acid. The results when nitric acid was used were not satisfactory. In both cases the acid obtained gave no constant melting point (the latter generally varying between  $140$  and  $144^{\circ}$ ), and consisted of a mixture of meta- and para-acid. Metatolyl phenyl ketone was also produced in each case. A partial separation was effected by means of the different solubility of the calcium salts in alcohol, but it was very imperfect. A good result was obtained by converting the mixed acids into benzhydrylbenzoic acid by reduction with sodium amalgam and water. The sodium salt of the meta-acid crystallised out, leaving that of the para-acid in solution. The metabenzhydrylbenzoic acid is easily reoxidised with chromic acid. *Metabenzoylbenzoic acid* is sparingly soluble in cold water, more easily in hot. Alcohol and ether dissolve it readily. It crystallises from acetic acid or water in needles, from dilute alcohol in scales. It dissolves in concentrated sulphuric acid without discoloration. It melts at  $161^{\circ}$ , and sublimes at a higher temperature. The *barium salt* is pretty freely soluble in water, sparingly so in absolute alcohol, and crystallises under varying circumstances with 2, 3, and 4 mols.  $H_2O$ . The *calcium salt* is soluble in water and alcohol; the *silver salt* forms a white amorphous powder almost insoluble in water. The *methyl ether*, prepared from the silver salt, crystallises in prisms soluble in alcohol and ether, and melting at  $62^{\circ}$ . A much better yield of benzoylbenzoic acid is obtained by oxidising the monobromine-derivative (prepared by passing the vapour of bromine into benzyltoluene heated to  $120$ — $130^{\circ}$ ) in place of the hydrocarbon.

*Metabenzhydrylbenzoic acid*,  $CHPh(OH).C_6H_4.COOH$ , obtained, as already mentioned, by the reduction of benzoylbenzoic acid, crystallises in small silky needles melting at  $121^{\circ}$ , and decomposing at a slightly higher temperature. This acid is easily soluble in alcohol, ether, and benzene, and dissolves in sulphuric acid to an orange solution. The *sodium salt*,  $C_{14}H_{11}O_3Na + 4H_2O$ , crystallises in fine white needles, melting at  $90^{\circ}$  in their water of crystallisation, which they lose at  $160$ — $180^{\circ}$ . It is more easily soluble in alcohol than in water. The *calcium salt* forms a crystalline powder containing 5 mols.  $H_2O$ . It is easily soluble in alcohol and ether. The *silver salt*,  $C_{14}H_{11}O_3Ag + H_2O$ , is precipitated as a white powder, which is slightly soluble in boiling water and crystallises from this solution in small needles.

*Metabenzylbenzoic acid*,  $CH_2Ph.C_6H_4.COOH$ , was obtained by the reduction of metabenzhydrylbenzoic acid. The reduction may be effected by the continued action of sodium amalgam on an alcoholic solution of the latter acid, but the reaction is *very* slow. The best method is to heat benzhydrylbenzoic acid with an excess of hydriodic acid (b. p.  $127^{\circ}$ ) in sealed tubes at  $170^{\circ}$  for three hours; the yield is very nearly equal to theory. Metabenzylbenzoic acid is easily soluble in

alcohol, ether, and chloroform, sparingly in cold, more easily in hot water, and crystallises from the latter in minute needles. From dilute alcohol, it crystallises in scales. It melts at  $107-108^{\circ}$ , and sublimes at a higher temperature. It dissolves in concentrated sulphuric acid without discoloration, and is oxidised by chromic acid to metabenzoylbenzoic acid. The *calcium salt* forms a crystalline powder containing 1 mol.  $H_2O$ , and is easily soluble in alcohol and water. The *barium salt* crystallises with  $4H_2O$ , and is soluble in water and alcohol. The *silver salt* forms a light white powder slightly soluble in boiling water and alcohol, and crystallising from these solutions in small needles.

The author also prepared metabenzylbenzoic acid by the action of aluminium chloride on  $CH_2Br.C_6H_4.COOH$  dissolved in benzene. Toluic acid was obtained by oxidising xylyl chloride prepared from ordinary xylene with nitric acid (1 vol. acid to 3 vols. water). This acid was then brominated at  $160-170^{\circ}$ , so as to insure the bromine entering the Me-group, and the crude benzylbenzoic acid was purified by conversion into the barium salt. The yield never exceeded 50 per cent. of theory, so that the reduction of the easily obtainable benzhydrylbenzoic acid is by far the better method for the preparation of this acid.

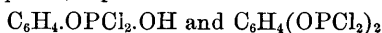
By the oxidation of Zinke's benzyltoluene (from benzyl chloride, toluene, and zinc-dust), and of the products of the action of water on benzyl chloride, small quantities of ortho- and para-benzoylbenzoic acid were obtained; in the latter case a trace of the meta-acid was also detected. Zinc chloride acting on a mixture of benzoic chloride and ethyl benzoate yielded a little ethyl metabenzoylbenzoate, but no ortho- or para-ether. When benzyl chloride was substituted for benzoic chloride in the last reaction, only condensation-products from the chloride were obtained.

*Metaphenyl tolyl ketone* is, as already mentioned, always amongst the products of oxidation of benzyl toluene. It is a colourless, slightly aromatic oil, boiling at  $314-316^{\circ}$  (col. in vapour and bar. 745 mm.). Its density at  $17.5^{\circ}$  is 1.088. It is miscible with alcohol, ether, benzene, chloroform, and acetic acid in all proportions.

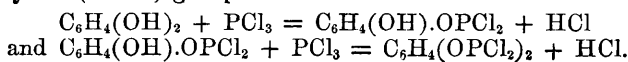
L. T. T.

**Quinone.** By B. SCHEID (*Annalen*, **218**, 195—231).—In order to throw some light on the constitution of the quinones, the author has studied the action of phosphorus pentachloride and oxychloride, acetic chloride, and other substances on it.

With quinone phosphorus pentachloride forms monochloroquinol, together with smaller quantities of dichloroquinol, the former of which is readily converted into monochloroquinhydrone. Phosphorus oxychloride gives monochloroquinol only. By the action of phosphorus pentachloride on quinol, a product intermediate between

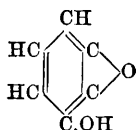


is obtained, formed by the successive replacements of hydroxyl groupings by the  $(OPCl_2)$  group thus:—

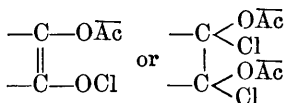


Quinol is reformed on decomposing the mixed product with water.

Acetic chloride acting on quinone or monochloroquinol produces monochlorodiacetylquinol, with evolution of hydrochloric acid, in accordance with the equation  $C_6H_4O_2 + 2\overline{Ac}Cl = C_6H_3Cl(O\overline{Ac})_2 + HCl$ . It would appear probable from the above reaction that quinone has an oxygen-atom combined with carbon only, whilst the other is combined with carbon and hydrogen (the hydroxyl-group). It would thus have the constitution of a glycide phenol, thus—



The other formulæ proposed for quinone, in which the oxygen is combined with the carbon as in a ketone, or the two oxygen-atoms are combined with another thus:  $\equiv C-O-O-C\equiv$ , would involve the intermediate formation of compounds—



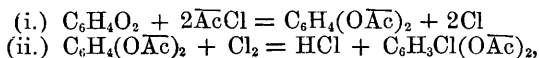
and the subsequent interchange of hydrogen for chlorine in the hydrocarbon grouping.

By the action of acetic chloride or anhydride on quinol, diacetylquinol is also formed.

Quinone was also treated with potash, water, carbon oxychloride, and sulphuryl hydroxychloride, but the results were unsatisfactory.

V. H. V.

**Quinone.** By O. HESSE (*Annalen*, **220**, 365—367).—Scheid (*Annalen*, **218**, 217) contends that the evolution of hydrochloric acid by the action of acetic chloride on quinone proves the presence of a hydroxyl-group in the latter body. The author believes that this reaction is rather to be explained according to the equations:



and is thus similar to the production of chloroquinol from quinone and hydrochloric acid. He believes that the acetyl-derivatives of quinone said to have been obtained, are really derivatives of quinol formed by the decomposition of quinone. Acetic anhydride brings about this decomposition only at temperatures above  $200^\circ$ , but quinone, in an aqueous solution of sodium acetate, is slowly decomposed at ordinary temperatures, a part being converted into quinol; the acetate, however, remains unchanged. The decomposition takes place more rapidly if the solution is heated.

L. T. T.

**Trichloroquinone-chlorimide, Tri- and Tetra-chloroquinone.**

By M. ANDRESEN (*J. pr. Chem.* [2], **28**, 422—436).—Former research has shown (Abstr., 1882, 400) that by the action of aniline on trichloroquinone, dichloroquinone-dianilide is formed, and not as Schultz and Knapp (*Annalen*, **210**, 181) have stated, monochloroquinone-dianilide. By the action of aniline on tetrachloroquinone and trichloroquinone-chlorimide dichloroquinone-dianilide is also formed, along with the compound monochlorodianilide-phenylquinoneimide,  $(?)C_6Cl(NHPh)_2ONPh$ . This latter substance is obtained in quantity by adding aniline to dichloroquinone-chlorimide in the proportion of 5 mols. to 1. It crystallises from hot alcohol in long needles melting at  $195^\circ$ . Nitrous acid passed into the alcoholic solution converts it into a nitroso-compound crystallising in green plates, which in pure alcohol are immediately reconverted into the original substances. Unlike dichloroquinone-dianilide it is not decomposed by boiling with alkalis in aqueous solution, but on adding alcohol a reaction does take place, and it dissolves to a red-coloured solution of a disodium compound,  $C_{24}H_{17}ClN_3ONa_2$ . On evaporation, this sodium compound crystallises in red needles, which dissolve in pure alcohol with immediate separation of the original substance. By the action of hydrochloric acid in alcoholic solution, it is decomposed with separation of aniline into monochloroquinone-dianilide, which, however, differs from that obtained by Schultz and Knapp.

Hydrochloric and hydrobromic acids have a reducing action on trichloroquinone-chlorimide. On treating the substance dissolved in pure benzene with dry hydrochloric acid gas, trichloroquinonimide hydrochloride is formed, whilst chlorine is given off. This body is decomposed by water into ammonium chloride and trichloroquinone. On treating trichloroquinone-chlorimide directly with hydrochloric acid in aqueous solution, it is decomposed into trichloroquinone, ammonium chloride, and chlorine, part of the chlorine being given off and part converting some of the trichloroquinone into tetrachloroquinone. Hydrobromic acid acts in an analogous way, yielding trichloroquinone, ammonium chloride, bromine, and some bromotrichloroquinone.

A. B.

**Diiodoquinone and Diiodoquinone-chlorimide.** By R. SEIFERT (*J. pr. Chem.* [2], **28**, 437—438).—Diiodoparanitrophenol (Korner, *ibid.*, 1868, 324) yields diiodoparamidophenol by reduction with tin and hydrochloric acid. If this is suspended in a slightly acid solution and treated with chloride of lime solution, it yields diiodoquinone-chlorimide,  $C_6H_2I_2<\overset{O}{N}>Cl$ , melting at  $123^\circ$ , but decomposing at a higher temperature. With dimethylaniline it yields diiodoquinone-dimethylanilide, analogous to trichloroquinone-dimethylanilide (Abstr., 1882, 400). Chromic mixture oxidises diiodoparamidophenyl sulphate to diiodoquinone,  $C_6H_2I_2O_2$ , crystallising from hot alcohol in yellow prisms, and melting at  $178^\circ$ . By boiling with stannous chloride, it yields diiodoquinol, crystallising from hot aqueous solution in long white needles, and melting at  $145^\circ$ ; ferric chloride reconverts it into the diiodoquinone. The author is continuing his research on these compounds.

A. B.

**Arbutin.** By H. SCHIFF (*Gazzetta*, 13, 538—513; also *Annalen*, 221, 365—379).—The author has already stated (*Gazzetta*, 11, 99; Abstr., 1881, 610) that he did not succeed in separating methylarbutin from arbutin, either by the use of solvents or by partial fusion of the natural mixture of these two glucosides. Afterwards he obtained methylarbutin by the action of methyl iodide on a solution of natural arbutin in caustic potash (*Ber.*, 15, 1841; and 1883, Abstr., 60); and in order to compare this methylarbutin with the natural compound and separate the latter from arbutin, he has endeavoured to introduce a higher alcohol-radicle into arbutin, and thereby transform it into a compound considerably less soluble than methylarbutin. The treatment of arbutin with isopentyl bromide (amyl bromide) did not yield the desired result, as oily bodies were formed at the same time, which impeded the crystallisation, and could not easily be removed. The isopentylarbutin produced in this reaction crystallised in needles and was resolvable into glucose and isopentylquinol, an oily liquid, convertible by cold dilute nitric acid into a nitro-derivative which crystallised in small yellow needles, melting at the heat of boiling water, and forming a dark orange-coloured crystalline compound with ammonia.

The separation of the methylarbutin was more easily effected by converting the arbutin into benzylarbutin, viz., by the action of benzyl bromide and potassium hydroxide on natural arbutin, whereby the benzylarbutin is precipitated almost completely in the form of a crystalline mass. The filtered solution is then evaporated and the methylarbutin is extracted from the residue with absolute alcohol, decolorised with animal charcoal, and purified by recrystallising it several times from water. Natural methylarbutin thus prepared, crystallises in long white needles, having, like the artificial compound, the formula  $C_{13}H_{18}O_7 \cdot H_2O$ , melting at  $174^\circ$ , and recrystallising at  $120-125^\circ$ . The artificially prepared compound, probably more free from impurities, melted at  $175-176^\circ$ . Natural methylarbutin does not give a blue colour with ferric chloride, does not reduce potassio-cupric solutions, and behaves in every way like the artificial compound, with which it is doubtless identical.

*Benzylarbutin*,  $C_{19}H_{22}O_7 \cdot H_2O = C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot O \cdot CH_2Ph \cdot H_2O$ , prepared as above, dissolves in 530 pts. water at  $23^\circ$ , much more freely in boiling water, and crystallises therefrom on cooling in branches of small colourless needles which melt at  $161^\circ$ , give off 1 mol.  $H_2O$ , and may be heated to  $250^\circ$  without alteration beyond a slight brown coloration. It does not reduce potassio-cupric solutions, unless previously heated with dilute sulphuric acid, in which case it is easily resolved into glucose and benzylquinol.

*Benzylquinol*,  $HO \cdot C_6H_4 \cdot OC_7H_7$ , thus prepared, separates almost completely on cooling, being much less soluble in cold water than benzylarbutin. It dissolves readily in alcohol, ether, benzene, and boiling water, and separates from the latter in large scales, having a brilliant silvery lustre, melting at  $121-122.5^\circ$ , recrystallises at about  $110^\circ$ , and is identical in every respect with the compound which Pellizzari has obtained by the action of benzyl bromide on quinol (p. 437 of this volume).

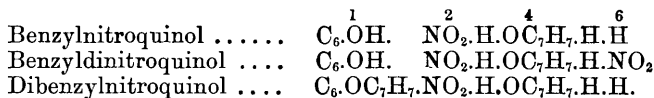


*Benzylnitroarbutin*,  $C_{19}H_{21}(NO_2)O_7$ , is prepared by gradually adding finely pulverised benzylarbutin to strong colourless nitric acid, avoiding all rise of temperature. It then dissolves readily and in large quantity without emission of red vapours, and the solution after some hours deposits a crystalline mass, which by two crystallisations from water containing a little acetic acid, yields benzylnitroarbutin in yellowish needles, acquiring a somewhat darker colour when dried in the air, especially in the ammoniacal atmosphere of a laboratory. It is less soluble in cold water than benzylarbutin. The crystals contain 1 mol. water, which they give off at  $110-115^\circ$ , and the anhydrous compound melts at  $142-143^\circ$ , at the same time turning brown and decomposing.

*Benzylnitroquinol*,  $HO.C_6H_3(NO_2).OC_7H_7$ , is formed by heating an aqueous solution of benzylnitroarbutin with dilute sulphuric acid, and crystallises from boiling water in long gold-coloured needles, melting with complete decomposition at  $156-158^\circ$ . With ammonia it forms a compound which crystallises in shining scales having the colour of cinnabar. The potassium-compound forms red needles.

When benzylquinol is treated with nitric acid, without previous separation from benzylarbutin, the process being otherwise conducted exactly as above directed, gold-coloured needles are obtained, agreeing with those just described in every respect, excepting that they melt at  $137^\circ$  without decomposition, the fused mass recrystallising as it cools.

The nitro-derivatives of benzylquinol obtained by the author, and that of dibenzylquinol obtained by Pellizzari (p. 437), may be represented by the following constitutional formulæ:—



H. W.

**Experiments on the Preparation of Nitrophenetol.** By H. KOLBE (*J. pr. Chem.* [2], 28, 62—63).—In a previous paper on “A Simple Method for Preparing Phenetol” (Abstr., 1883, 1113), it was remarked that probably nitrophenetol might be obtained by heating a salt of hydrogen ethyl sulphate with sodium nitrophenate as easily as phenetol is prepared from potassium ethyl sulphate and sodium phenate. On making the experiment in open apparatus, it was found that but very little product was obtained, either from ortho- or from para-nitrophenol, and on employing sealed tubes, these exploded before the temperature had reached  $150^\circ$ .

H. B.

**Ethylene Ethers of the Nitrophenols and Hydroxybenzoic Acids.** By E. WAGNER (*J. pr. Chem.* [2], 27, 199—230).—Weddige (Abstr., 1881, 1136) has shown that when ethylene bromide acts on the sodium-derivative of mononitrophenol, two different compounds are produced, the ether,  $(NO_2.C_6H_4O)_2C_2H_4$ , and the bromhydrin,  $NO_2.C_6H_4O.C_2H_4Br$ . It is the former compound and some of its derivatives which form the subject of the first part of the author's paper.

*Ethylene Amidophenyl Ethers.*—The ethylene nitrophenyl ethers

used in preparing these compounds were obtained by heating ethylene bromide (1 mol.) with the sodium nitrophenate (2 mols.) at  $140^{\circ}$ . The product is treated with alcohol, the insoluble residue washed with cold water to remove sodium bromide, and then with boiling alcohol to remove the last traces of the bromhydrin produced at the same time; the nearly pure nitro-ether, which remains as a white pulverulent mass, is sparingly soluble in benzene and almost insoluble in cold alcohol. The melting points of the three isomerides are as follows:—

Ethylene orthonitrophenyl ether .....	163°
Ethylene metanitrophenyl ether .....	139°
Ethylene paranitrophenyl ether .....	143°

The amido-ethers are obtained from the corresponding nitro-ethers by reduction with tin and hydrochloric acid; as the mixture cools, the tin double salt of the amido-ether separates in large colourless crystals, which are sparingly soluble in cold water, but easily in hot water acidified with hydrochloric acid. The dilute solution of the tin salt is decomposed by hydrogen sulphide, and filtered from the stannous sulphide, which must be well washed with boiling water to dissolve out adhering amido-hydrochloride, and the filtrate and washings concentrated as rapidly as possible, as the amido-compound is easily oxidised. As the dark solution cools, it deposits the hydrochloride of the ethylene amido-ether in tufts of long plates in the case of the ortho-, and needles in the case of the meta-compound. On adding sodium carbonate to the aqueous solution of the crude hydrochloride, the base is separated in the free state, and after being collected on a vacuum-filter and washed with a little water, it is purified by one or two crystallisations from hot absolute alcohol. *Ethylene orthamidophenyl ether*,  $(\text{NH}_2\cdot\text{C}_6\text{H}_4\text{O})_2\text{C}_2\text{H}_4$ , crystallises from hot alcohol or water in lustrous white or reddish rhombic plates which melt at  $128^{\circ}$ . It is insoluble in cold water, but easily soluble in most of the usual solvents. It is diacid, and dissolves easily in acids, forming crystalline salts. *Ethylene paramidophenyl ether* crystallises in needles which melt at  $168\text{--}172^{\circ}$ . It is easily soluble in benzene, but differs from its isomeride in being sparingly soluble in chloroform and ether. *Ethylene metamidophenyl ether* forms reddish prisms which melt at  $135^{\circ}$ , and resembles the para-compound. The reactions of these three bases with various reagents are given in the accompanying table.

	Ortho-ether.	Para-ether.	Meta-ether.
$\text{H}_2\text{SO}_4$ , cold .....	Blue-black colour..	Indigo-blue ..	Dark-brown coloration
$\text{H}_2\text{SO}_4$ , hot .....	Dirty violet colour	Ditto	Dark-brown coloration
$\text{Fe}_2\text{Cl}_6$ .....	Sepia brown ..	Cherry-red colour	Brownish-black
Chromic mixture...	Alizarin-red colour	Intense blue-violet coloration and formation of quinone	Ditto

*Ethylene orthamidophenyl ether hydrochloride* is obtained pure by

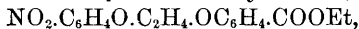
dissolving the base in warm dilute hydrochloric acid; on cooling, it crystallises out in stellate groups of silvery, flat needles, containing 2 mols.  $\text{H}_2\text{O}$ . When heated at  $110\text{--}150^\circ$ , part of the salt sublimes in woolly needles, but the greater part is destroyed. On adding platinic chloride to the aqueous solution of the hydrochloride, a golden-yellow crystalline precipitate of the platinochloride is produced, but it rapidly alters and decomposes. The other salts of the base may be prepared in a manner similar to the hydrochloride. Of these the sulphate is the least soluble in water, whilst the acetate is very soluble. The oxalate and nitrate were both prepared, and are crystalline. *Ethylene acetyl-orthamidophenyl ether*,  $(\text{NHAc.C}_6\text{H}_4\text{O})_2\text{C}_2\text{H}_4$ , is formed by the action of acetic anhydride on the base; the brown crystalline product is treated with alcohol to remove unaltered base, and crystallised from boiling aniline. It forms long needles which melt at  $226^\circ$ . It may also be prepared by heating the base with excess of glacial acetic acid at  $160^\circ$  for some hours. When heated in a retort it is decomposed, a dark yellow oil passing over, whilst a carbonaceous residue is left. The distillate consists of the free base, and a yellow oil of penetrating odour and very high boiling point, but no anhydro-base is formed; attempts to obtain a body of this class by the action of benzaldehyde on the base and on its hydrochloride were also unsuccessful.

*Ethylene paramidophenyl ether hydrochloride*, prepared in a similar manner to the salt of the ortho-base, crystallises in long colourless slender needles, which contain no water of crystallisation; it is easily soluble in water. The *sulphate* is sparingly soluble; the nitrate and oxalate were also prepared.

*Ethylene metamidophenyl ether hydrochloride* closely resembles the para-salt. The sulphate, nitrate, and oxalate were also prepared. On adding a concentrated solution of the nitrate of the meta-base to a solution of diazobenzene nitrate, it becomes first yellow, then red, and after a time deposits a red amorphous substance analogous to chrysoidine in its properties, capable of dyeing silk orange-yellow. On adding sodium carbonate to a hot solution of the dye, a few dirty yellow flocks are thrown down, which, after recrystallisation from boiling water, form yellow scales melting at  $133\text{--}136^\circ$ : analysis, however, showed that they were merely the original metamidophenyl ether coloured by the yellow azo-dye.

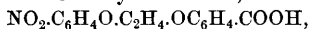
Part II of the paper gives a description of ethylenephenol-oxybenzoic acids and some of their derivatives.

*Ethylic ethylene-orthonitrophenol-orthoxybenzoate*,\*



is prepared by digesting ethylic potassium salicylate with bromethylene orthonitrophenyl ether in alcoholic solution for some days; the alcoholic solution is then poured off from the solid residue consisting of salicylethylene orthonitrophenol ether and potassium bromide, the alcohol removed by evaporation, and the residue freed from ethylic

\* Ethylene-orthonitrophenol-orthoxybenzoic acid,



might be more consistently named orthonitrophenoxethylene-orthoxybenzoic acid, and the nomenclature of the other acids changed in a similar manner.—C. F. G.

salicylate by steam-distillation; the yellow viscous oily residue contains the ether in small quantity; it may be extracted by warm dilute alcohol, but the author was unable to obtain it in a state of purity. It is a yellow powder, consisting of microscopic needles which melt at about  $100^{\circ}$ , insoluble in water, but soluble in most of the usual solvents. It is saponified by boiling with soda-solution, yielding a sodium salt of the corresponding acid, but the greater portion of the substance undergoes further decomposition. The acid may, however, be obtained from the yellow viscous oil previously mentioned by heating it for several days at  $130$ – $140^{\circ}$  with concentrated hydrochloric acid (6–8 parts), repeating the treatment several times. On treating the oily product with soda, the acid is dissolved, and may be precipitated by acids in reddish-brown flocks, which crystallise from hot alcohol in small yellow needles melting at  $142$ – $148^{\circ}$ . The yield, however, is very small.

When the solid residue of potassium bromide and *salicylethylene orthonitrophenol ether*,  $\text{OH.C}_6\text{H}_4.\text{COO.C}_2\text{H}_4.\text{C}_6\text{H}_4.\text{NO}_2$ , mentioned above, is washed with cold water, the ether is left behind, and may be purified by repeated crystallisation from boiling alcohol, when it is obtained in transparent yellow plates melting at  $106^{\circ}$ . It is decomposed by soda solution or when heated with concentrated hydrochloric acid, salicylic acid and an oily body being produced. When treated with tin and hydrochloric acid it dissolves easily, yielding salicylic acid and the hydrochloride of a base,  $\text{NH}_2.\text{C}_6\text{H}_4.\text{O.C}_2\text{H}_4.\text{OH}$ . The free base forms small colourless plates which melt at  $90^{\circ}$ , and rapidly become brown on exposure to the air.

When ethylene-orthonitrophenol-oxybenzoic acid is reduced with tin and hydrochloric acid, it yields the salt of the corresponding amido-acid, from which the hydrochloride may be obtained in the usual way; this forms small colourless needles melting at  $177^{\circ}$ , whilst the free amido-acid crystallises in small thick colourless prisms melting at  $110^{\circ}$ .

*Ethylic Ethylene-paranitrophenol-orthoxybenzoate*, obtained from bromethylene paranitrophenol ether in a manner similar to the corresponding ortho-compound, crystallises in long thick pale yellow needles melting at  $81^{\circ}$ , whilst the free acid forms long colourless needles melting at  $132^{\circ}$ ; its salts are colourless. The *salicylethylene paranitrophenyl ether*, corresponding in composition, mode of formation, and properties with the isomeric ortho-compound previously described, melts at  $131^{\circ}$ .

Ethylic potassium-parahydroxybenzoate reacts sharply with bromethylene ortho- and para-nitrophenyl ethers, yielding a series of compounds analogous to those obtained with salicylic acid.

*Ethylic ethylene-orthonitrophenol-paroxybenzoate* forms yellow lustrous plates melting at  $103^{\circ}$ ; it yields orthonitraniline when heated with ammonia at  $140^{\circ}$ . The free acid obtained by heating the ethylic salt with hydrochloric acid crystallises in colourless needles melting at  $205$ – $207^{\circ}$ . The amido-acid forms broad needles melting at  $185^{\circ}$ .

*Ethylic ethylene-paranitrophenol-paroxybenzoate* melts at  $131^{\circ}$ , and the free acid at  $218^{\circ}$ ; it is reduced by tin and hydrochloric acid, but the corresponding amido-acid could not be isolated.

*Ethyllic ethylene-phenolparoxybenzoate*,  $\text{OPh.C}_2\text{H}_4.\text{OC}_6\text{H}_4.\text{COOEt}$ , is formed by the action of bromethylene phenyl ether on ethylic potassium-parahydroxybenzoate; it crystallises in colourless shining plates which melt at  $81^\circ$ , and on saponification yields the potassium salt of the ethylene-phenolparoxybenzoic acid. The free acid crystallises from hot alcohol in long silky needles melting at about  $196^\circ$ , sparingly soluble in benzene and chloroform. The properties of the various isomerides described in the paper are there given in tabular form for comparison. C. E. G.

**Benzyllic Ethers of the Dihydroxybenzenes.** By G. PELLIZZARI (*Gazzetta*, **13**, 501—507; also *Annalen*, **221**, 365—379).—**1. BENZYLQUINOLS.**—These compounds,  $\text{C}_6\text{H}_5(\text{C}_7\text{H}_7)_2\text{O}$  and  $\text{C}_6\text{H}_4(\text{C}_7\text{H}_7)_2\text{O}_2$ , are formed when quinol dissolved in a small quantity of alcohol, and benzyl bromide, in molecular proportions, are made to act on one another in presence of alcoholic potash. The action commences at ordinary temperatures, and is quickly completed on heating, the solution turning brown and depositing crystals of potassium bromide. When all the benzyl bromide is decomposed, a small quantity of sulphuric acid is added and then water, whereby a crystalline substance is thrown down, part of which is dissolved out by alcohol, together with the whole of the colouring matter, while a nearly white substance remains behind.

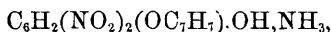
*Monobenzylquinol*,  $\text{C}_6\text{H}_4(\text{OC}_7\text{H}_7).\text{OH}$  [ $\text{OC}_7\text{H}_7 : \text{OH} = 1 : 4$ ], is the portion of the product which dissolves in alcohol. It may be freed from colouring matter by recrystallisation from boiling alcohol, and is deposited therefrom on cooling in silvery laminae melting at  $122^\circ$ , very soluble in alcohol, ether, chloroform, and benzene, slightly soluble in boiling water, extremely soluble in aqueous potash. The compound thus prepared agrees in every respect with the benzylquinol which H. Schiff obtained from benzylarbutin.

*Dibenzylquinol*,  $\text{C}_6\text{H}_4(\text{OC}_7\text{H}_7)_2$ , is the white crystalline substance above mentioned, sparingly soluble in alcohol. When dissolved in boiling alcohol, it separates on cooling in beautiful shining laminae, melting at  $130^\circ$ , insoluble in water and in aqueous potash, moderately soluble in benzene, ether, and chloroform.

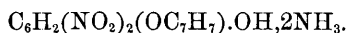
*Benzylidinitroquinol*,  $\text{C}_6\text{H}_2(\text{NO}_2)_2(\text{OC}_7\text{H}_7).\text{OH}$ , is prepared by throwing pulverised monobenzylquinol by small portions into cooled strong nitric acid, and crystallises from alcohol in splendid golden-yellow laminae, soluble in ether, benzene, and boiling water, melting at  $137^\circ$ . When treated with potash, it forms red needles of a potassium derivative which, when left in a vacuum, give off 1 mol. crystal-water, their cinnabar-colour changing at the same time to a dark-red colour, with splendid metallic reflex. On exposure to the air, the compound recovers its molecule of water and its original colour. It detonates strongly when heated.

When dry ammonia-gas is passed over the dinitro-compound contained in a tube, the substance becomes heated and assumes a fine blood-red colour, which, if the passage of the gas be continued, slowly changes to a brick-red; but on subsequently passing a current of dry air over the product, the original blood-red colour is restored. These

changes indicate the formation of two different compounds, and analysis shows that the brick-red substance has the composition



while the blood-red compound contains a double proportion of ammonia, being represented by the formula



The monammonia compound is stable, and may be recrystallised without alteration, whereas the diammonia compound is stable only in an atmosphere of ammonia.

*Dibenzylnitroquinol*,  $\text{C}_6\text{H}_3(\text{NO}_2)(\text{OC}_7\text{H}_7)_2$ , is formed on throwing finely pulverised dibenzylquinol into strong nitric acid, and applying a gentle heat, whereupon the mass assumes a lemon-yellow colour, and when crystallised from alcohol, yields long yellow needles of the dinitro-compound. This body does not contain a free hydroxyl-group, and consequently does not yield any metallic derivatives.

On treating the two nitro-compounds dissolved in acetic acid with stannous chloride, the formation of amido-compounds was indicated by the red colour which the products gave with furfural; but their stannochlorides were too soluble, and their hydrochlorides too unstable, to admit of quantitative determination.

**BENZYL-RESORCINOLS.**—*Dibenzylresorcinol*,  $\text{C}_6\text{H}_4(\text{OC}_7\text{H}_7)_2$  [1 : 3], is prepared like the corresponding quinol derivative, and separates from solution in hydrochloric acid, on addition of water, as a very dense syrupy mass, which dissolves in alcohol, and is deposited therefrom in white shining scales melting, after purification, at 79°.

The product thus obtained did not appear to contain any monobenzylresorcinol, but this compound may be obtained, together with the dibenzyl-derivative, by leaving resorcinol and benzyl bromide in molecular proportion in contact with aqueous potash, and agitating the mixture at intervals for several days till all the benzyl bromide is decomposed.

In this manner, a semi-fluid mass is formed, containing dibenzylresorcinol and a supernatant alkaline liquid, from which acids throw down yellowish flakes of a compound having nearly the composition of *monobenzylresorcinol*,  $\text{C}_6\text{H}_4(\text{OC}_7\text{H}_7).\text{OH}$ . Analysis 78.55 C and 6.00 H; calc. 78.00 C and 6.00 H. This substance, after washing on a filter, forms a solid amorphous mass, soluble in alcohol, benzene, ether, acetic acid, and chloroform, but does not separate from these solutions in crystalline form. Both the benzylresorcinols become resinised on treatment with strong nitric acid.

**DIBENZYL CATECHOL**,  $\text{C}_6\text{H}_4(\text{OC}_7\text{H}_7)_2$  [1 : 2], prepared like its analogues above described, crystallises from alcohol in needles having a very faint yellow colour, and melting at 61°. It dissolves in the ordinary solvents, and is converted by nitric acid into a nitro-derivative, which crystallises in opaque yellow needles melting at 98°.

The portion of the product which is soluble in aqueous potash separates therefrom, on addition of an acid, as a somewhat mobile liquid, which decomposes at about 200°, but may be distilled with

steam. With ferric chloride, it gives a faint violet coloration, indicating the presence of a hydroxyphenol: hence it is probably monobenzylcatechol. Strong nitric acid converts it into a solid mass, which crystallises from alcohol in yellow shining needles melting at  $129^{\circ}$ .  
H. W.

**Synthetical Researches in the Glucoside Group.** By A. MICHAEL (*Amer. Chem. J.*, **5**, 171—182; cf. Abstr., 1879, 1038).—*Tetracetylphenolglucoside*,  $C_6H_7O(OPh)(O\bar{Ac})_4$ , is prepared by heating a mixture of 1 part of phenolglucoside with 5 parts of acetic anhydride and 2 parts of fused sodium acetate on the water-bath for three hours. It crystallises in long white glistening needles, is insoluble in cold, sparingly soluble in hot water and in cold alcohol, readily soluble in hot alcohol. It seems to suffer slight decomposition when the alcoholic solution is boiled for a few minutes, as the odour of acetic ether becomes decidedly perceptible. It does not reduce Fehling's solution, except on long-continued boiling.

*Synthesis of Salicin from Synthetical Helicin.*—Lisensko having shown that helicin prepared from salicin is reconverted into the latter by the action of sodium-amalgam (*Zeitsch. Chem.*, 1864, 577), the author thought it advisable to repeat the experiment with helicin synthesised from sodium salicylaldehyde and acetochlorhydrate, and finds the product to be identical with natural helicin. This is the first known instance of the synthesis of a natural glucoside.

By the action of dipotassium salicylate on acetochlorhydrate there is obtained, not as was expected, the glucose of salicylic acid, but a body,  $C_{26}H_{30}O_{15}$ , standing to it in the relation of an anhydride or ether. It crystallises in long white needles, melts at  $184$ — $185^{\circ}$ , is insoluble in cold, sparingly soluble in hot water or in cold alcohol, readily soluble in warm alcohol. It does not reduce Fehling's solution. It is insoluble in cold aqueous ammonia, but on boiling a gradual solution is effected; it is also soluble in aqueous potash; these solutions reduce Fehling's solution, and probably contain salicylglucoside. The acetyl-compound,  $C_{26}H_{22}O_{15}\bar{Ac}_8$ , forms long white needles, melts at  $110$ — $111^{\circ}$ , is insoluble in water, soluble in alcohol.

*Synthesis of Methylarbutin.*—The potassium-derivative of quinolmonomethylin,  $C_6H_4(OMe).OK$ , was prepared by mixing equivalent quantities of potassium ethoxide and quinolmonomethylin in alcoholic solution and adding large excess of ether, when the potassium compound is precipitated as a white crystalline powder. This is dissolved in absolute alcohol, acetochlorhydrate added, and the solution allowed to stand for several days, the deposited potassium chloride filtered off, and the liquid allowed to evaporate spontaneously. *Methylarbutin*,  $2C_{13}H_{18}O_7 + H_2O$ , so obtained, crystallises in long, colourless, silky needles, melts at  $168$ — $169^{\circ}$ , and resolidifies at  $137$ — $138^{\circ}$ , is readily soluble in water and alcohol, insoluble in ether. It is not precipitated by basic lead acetate nor copper salts, and does not reduce Fehling's solution, but is rapidly decomposed into dextrose and quinol monomethylin on digestion with dilute acids. It is distinguished from arbutin by not giving a blue coloration with ferric chloride; this is in

accordance with the formula  $C_6H_{11}O_5.O.C_6H_4.OMe$ , derived from its method of preparation, and shows the absence of hydroxyl in the aromatic group.

A. J. G.

**Hydrazine Compounds of Phenol and Anisoil.** By H. REISENEGGER (*Annalen*, **221**, 314—332).—Attempts to prepare hydrazine phenols from the potassium salts of ortho- and para-hydrazine-phenolsulphonic acids gave negative results. *Orthohydrazinanisoil*, obtained from orthanisidine by a method analogous to that by which E. Fischer prepared phenylhydrazine, crystallises in white needles which decompose on exposure to the air. The crystals melting at  $43^\circ$  are soluble in alcohol, ether, and benzene. The *hydrochloride*,



*sulphate*, and *oxalate* are crystalline salts, soluble in hot water. The *picrate* forms yellow plates which detonate when quickly heated. *Monacetic orthohydrazinanisoil* crystallises in white needles which melt at  $125^\circ$ . The compound *carbamide*,  $OMe.C_6H_4.N_2H_2.CONH_2$ , prepared by the direct union of ethyl isocyanate and hydrazineanisoil, forms needle-shaped crystals, which melt at  $110^\circ$ .

W. C. W.

**Hydrazines of Cinnamic Acid.** By E. FISCHER and H. KUZEL (*Annalen*, **221**, 261—297).—Methods for preparing many of the compounds described in this paper have already appeared in this Journal (Abstr., 1881, 598; 1883, 812, 1132). *Ethylamidocinnamic acid*, melting at  $125^\circ$ , dissolves in alcohol, ether, and carbon bisulphide, forming a yellow solution which exhibits a green fluorescence. It unites with acids and alkalis, yielding crystalline salts which are very soluble in water.

*Diethylamidocinnamic acid* forms large crystalline plates of a pale lemon colour, and melts at  $124^\circ$ . It is freely soluble in alcohol, ether, and carbon bisulphide. This substance combines with alkalis, and also unites with acids to form colourless crystalline salts which dissolve easily in water.

*Nitroso-orthoethylamidocinnamic acid*,  $NOEtN.C_6H_4.CH:CH.COOH$ , forms pale-yellow plates, which melt at  $150^\circ$  with decomposition. It dissolves readily in ether, alcohol, chloroform, and in hot water, and also in solutions of alkalis or alkaline carbonates, but not in acids.

Friedländer and Wienberg have pointed out (*Ber.*, **15**, 2104) that an alkaline solution of orthoethylamidocinnamic acid is converted into the hydro-acid by sodium-amalgam. If the cold solution is cautiously neutralised with dilute sulphuric acid, ethylamidocinnamic acid is precipitated. The precipitate dissolves easily in excess of sulphuric acid, and is converted into ethylhydrocarbostyryl by warming the solution. On adding sodium nitrite to the solution of ethylamidocinnamic acid in dilute sulphuric acid, the *nitroso*-compound,  $NOEtN.C_6H_4.C_2H_4.COOH$ , is obtained. It crystallises in colourless plates which melt at  $78^\circ$  and decompose at  $150^\circ$ . The crystals dissolve freely in ether, benzene, alcohol, and alkalis.



The hydrochloride of orthodiazocinnamic acid is a yellow crystalline powder, which detonates when heated. The nitrate,  $C_9H_7O_2N_2.NO_3$ , crystallises in colourless prisms resembling the hydrochloride. Both these salts dissolve in warm water, but on boiling the solutions nitrogen is evolved and orthocumaric acid is formed. The best yield of orthocumaric acid is obtained from the sulphate.

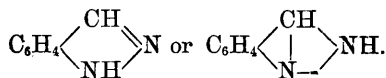
*Hydrazinecinnamic acid*,  $NH_2.NH.C_6H_4.C_2H_2.COOH$ , is best prepared by passing moist hydrochloric acid gas over sodium hydrazinesulphonate. When the salt acquires a brown colour, the excess of hydrochloric acid is expelled by a current of air and the residue is dissolved in warm water; on the addition of sodium acetate, a small quantity of resin separates, and is removed by filtration. Sodium acetate is again added, and the liquid evaporated to half its volume, when the acid is deposited in pale yellow crystals which are almost insoluble in alcohol, ether, and benzene. They are sparingly soluble in hot water, but the solution decomposes on evaporation. Hot glacial acetic acid dissolves hydrazinecinnamic acid, and the solution bleaches indigo and litmus.

*Orthohydrazinecinnamic anhydride*, which has been previously described (Abstr., 1881, 598), has not yet been directly prepared from the acid. The name "amidocarbostyryl" proposed for this compound has been abandoned, since Friedländer has shown that

carbostyryl has the constitution  $C_6H_4 \begin{array}{c} \text{CH:CH} \\ \diagdown \quad \diagup \\ \text{N} \end{array} \text{C.OH}$ , and the constitution of this anhydride is represented by the formula  $C_6H_4 \begin{array}{c} \text{CH:CH} \\ \diagdown \quad \diagup \\ \text{N(NH}_2\text{)} \end{array} \text{CO}$ .

Hydrazinecinnamic acid melts at  $146^\circ$ , and decomposes into acetic acid and indazole,  $C_6H_4(NHNH_2).C_2H_4.COOH = C_7H_6N_2 + C_2H_4O_2$ .

Indazole crystallises in colourless needles which melt at  $146.5^\circ$ , and sublime rapidly at  $100^\circ$ . It is soluble in alcohol, ether, hot water, and in dilute hydrochloric acid. It is precipitated from the acid solution by alkalis. Indazole yields a nitroso-compound. Its constitution may probably be represented as



Sodium hydrazinecinnamosulphonate is reduced by the action of sodium-amalgam to a salt of the hydro-acid, which forms colourless crystals freely soluble in water. On the addition of hydrochloric acid to the solution decomposition ensues, and *hydrazinehydrocinnamic anhydride* or *amidohydrocarbostyryl*,  $C_6H_4 \begin{array}{c} \text{CH}_2:\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{N(NH}_2\text{)} \end{array} \text{CO}$  is formed.

It is deposited in colourless plates melting at  $143^\circ$ , on the addition of an alkali to the solution. Amidohydrocarbostyryl is soluble in hot water and dilute acids. It combines with strong hydrochloric acid to form the hydrochloride  $C_9H_{10}N_2O.HCl$ , which crystallises in colourless prisms, soluble in water and alcohol. The base reduces alkaline silver solutions, but does not reduce Fehling's solution.

Hydrocarbostyryl is precipitated on the addition of sodium nitrite to an acid solution of amidohydrocarbostyryl.

*Ethylamidohydrocarbostyryl*,  $C_6H_4<\begin{smallmatrix} CH_2.CH_2.CO \\ -N(NEtH)- \end{smallmatrix}>$ , prepared by the action of ethyl iodide on an alcoholic solution of amidohydrocarbostyryl, forms colourless crystals melting at  $74^\circ$ , which are freely soluble in alcohol, ether, and chloroform. It unites with mineral acids to form salts which are very soluble in water. The nitrosamine is an oily liquid.

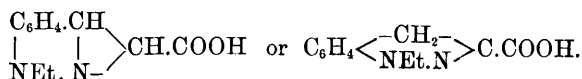
*Ethylquinazolcarboxylic acid* (Abstr., 1883, 812) is deposited from an aqueous solution in colourless plates which melt at  $131^\circ$ . On adding light petroleum to the solution of the acid in chloroform, it is precipitated in slender plates which melt at  $126^\circ$ . These crystals slowly change into the first modification.

Ethylquinazolcarboxylic acid forms crystalline compounds with bases and with acids. The crystalline hydrochloride, formed by passing hydrochloric acid gas into an ethereal solution of the carboxylic acid, is decomposed by water.

*Monobromethylquinazolcarboxylic acid*,  $C_{11}H_{11}N_2O_2Br$ , crystallises in colourless needles which melt at  $173^\circ$  with decomposition. It is freely soluble in alcohol and ether. The *dibromo-derivative*, melting at  $196^\circ$ , is less soluble in alcohol, ether, and chloroform than the preceding compound. The sodium salt is sparingly soluble in sodium hydroxide. It is deposited from a strongly alkaline solution in white plates. The bromine is eliminated by the action of sodium-amalgam.

*Ethylquinazole* (*loc. cit.*) unites with methyl iodide to form the compound  $C_{10}H_{12}N_2MeI$ , which is deposited from an alcoholic solution in highly refractive needle-shaped crystals melting at  $192^\circ$  with decomposition.

The constitution of ethylquinazole is probably



*Ethylhydrocarbostyryl*,  $C_6H_4<\begin{smallmatrix} CH_2.CH_2 \\ NEt.NH \end{smallmatrix}>CO$ , the isomeride of ethylamidohydrocarbostyryl, has been previously described (Abstr., 1883, 1132).  
W. C. W.

**Action of Benzaldehyde and Sulphuric Acid on a Mixture of Aniline and Nitrobenzene.** By G. MAZZARA (*Gazzetta*, 13, 527—529).—By this reaction the author obtained a base, the composition of which he has not yet determined. Its hydrochloride forms garnet-red crystals, dissolving freely in alcohol, with violet coloration, and in water. The solutions, however, as well as those obtained with sulphuric acid, do not leave crystalline salts on evaporation. Picric acid produces in the hydrochloric solutions a reddish hydrated precipitate soluble in alcohol. The hydrochloric solution gives precipitates with mercuric chloride and potassium dichromate. Platinic chloride forms a reddish-yellow precipitate in concentrated

solutions of the hydrochloride, and in aqueous solutions a brown precipitate containing water of crystallisation. H. W.

**Reaction of Ethyl Acetoacetate with Aldehydes.** By L. CLAISEN and F. E. MATTHEWS (*Annalen*, 218, 170—185).—A continuation and extension of former researches (Abstr., 1881, 405). The alkyl salts of acetoacetic acid react with aldehydes with elimination of water and substitution of the hydrogen-atom in the methylenic group by the hydrocarbon residue of the aldehyde, thus giving rise to substances of generic formula  $\text{CHR}:\text{C}(\text{COOEt})\cdot\text{COMe}$ . Less generally a hydrogen-atom in the methyl-group is replaced, and compounds of formula  $\text{CR}_2(\text{COOEt})\cdot\text{CO}\cdot\text{CH}:\text{CHR}$  are obtained. Further, all attempts to replace the hydrogen at once in the methyl and the methylenic group have been unsuccessful. *α*-Ethyl acetoacetonate,  $\text{CHMe}:\text{C}\overline{\text{Ac}}\cdot\text{COOEt}$ , is easily obtained by passing hydrochloric acid into a mixture of ethaldehyde and ethyl acetoacetate, when the condensation-product separates out as a colourless oil boiling at  $210^\circ$  (sp. gr. = 1.0225); it resembles the crotonic derivatives in odour. It is easily reconverted into aldehyde and ethyl acetoacetate; it takes up a molecule of bromine to form a viscid *dibromide*, which cannot be distilled.

*Ethyl acetisobutylideneacetate*,  $\text{C}_6\text{H}_8(\text{C}_4\text{H}_8)\text{O}_3$ , from isobutaldehyde and ethyl acetoacetate, is a colourless liquid boiling at  $219\text{--}222^\circ$ , possessing a peppermint-like smell.

*Ethyl acetisamylideneacetate*,  $\text{C}_6\text{H}_8(\text{C}_5\text{H}_{10})\text{O}_3$ , from valeraldehyde and ethyl acetoacetate, is a colourless liquid boiling at  $237\text{--}241^\circ$ , sp. gr. 0.9612.

*Ethyl acetotrichlorethylideneacetate*,  $\text{C}_6\text{H}_8(\text{C}_2\text{HCl}_3)\text{O}_3$ , from chloral and ethyl acetoacetate, is a viscid colourless liquid, smelling faintly of chlorine; sp. gr. 1.342; it can be distilled in a vacuum, but under ordinary pressure is decomposed with evolution of hydrochloric acid.

*Ethyl acetofurfuralacetate*,  $\text{C}_6\text{H}_8(\text{C}_5\text{H}_4\text{O})\text{O}_3$ , from furfuraldehyde and ethyl acetoacetate in presence of acetic anhydride, boils under a pressure of 30 mm. at  $188^\circ$ ; it forms large glistening crystals melting at  $62^\circ$ , and easily soluble in alcohol, chloroform, and benzene.

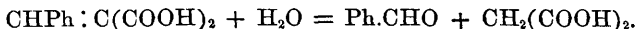
*Ethyl acetobenzylideneacetate*,  $\text{CHPh}:\text{C}\overline{\text{Ac}}\cdot\text{COOEt}$ , from benzaldehyde and ethyl acetoacetate, is a colourless tasteless strongly refractive oil, boiling at  $295^\circ$ ; on standing it crystallises in four- or six-sided tables. It takes up a molecule of bromine to form a dibromide,  $\text{C}_{13}\text{H}_{14}\text{O}_3\text{Br}_2$ , which crystallises in short colourless needles. Under certain conditions, a mixture of two isomeric chlorhydrins of ethyl acetobenzylideneacetate can be obtained, the one crystallising in prisms melting at  $41^\circ$ , easily soluble in alcohol and ether; the other crystallising in rhombohedrons melting at  $71^\circ$ , and equally soluble in the same menstrua.

The formation of two isomeric products can be explained by supposing that at first an intermediate chlorhydrin is produced,  $\text{CHPhCl}\cdot\text{CH}\overline{\text{Ac}}\cdot\text{COOEt}$ , and then is decomposed into the above-mentioned ethyl acetobenzylidenoacetate and hydrochloric acid, which subsequently recombine to form ethyl acetobenzylchloracetate, thus:  $\text{CHPh}:\text{C}\overline{\text{Ac}}\cdot\text{COOEt} + \text{HCl} = \text{CH}_2\text{Ph}\cdot\text{C}\overline{\text{Ac}}\text{Cl}\cdot\text{COOEt}$ . From these

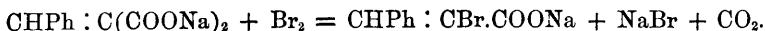
results it is probable that in all cases an intermediate chlorhydrin is first produced.

*Ethyl cinnamylethylacetate*,  $\text{CHPh}:\text{CH}.\text{CO}.\text{CHEt}.\text{COOEt}$ , is formed when the mixture of benzaldehyde and ethyl acetoacetate, which has been saturated with hydrochloric acid, is allowed to stand for a week or more. As it could not be obtained in a satisfactory state of purity, it was converted into the analogous *diethyl-derivative*,  $\text{CHPh}:\text{CH}.\text{CO}.\text{C}(\text{Et})_2.\text{COOEt}$ . This crystallises in triclinic prisms which melt at  $101^\circ$ ; it is easily soluble in chloroform and ether, sparingly soluble in alcohol. It combines with bromine to form a dibromide,  $\text{C}_{17}\text{H}_{12}\text{O}_3\text{Br}_2$ , which crystallises in prisms melting at  $55^\circ$ , easily soluble in alcohol and petroleum. V. H. V.

**Action of Benzaldehyde on Malonic Acid and its Ethylic Salt.** By L. CLAISEN and L. CRISMER (*Annalen*, **218**, 129—144).—In a preliminary notice, Claisen has described (Abstr., 1881, 405) a condensation-product of benzaldehyde and ethyl malonate, viz., ethyl benzalmalonate,  $\text{CHPh}:\text{C}(\text{COOEt})_2$ . In the present communication a fuller account is given of this substance and of the corresponding carboxylic acid,  $\text{CHPh}:\text{C}(\text{COOH})_2$ . This cinnamic and carboxylic acid resembles dicarbontetracarboxylic acid, and differs from other acids in which the two carboxyl-groups are attached to the same carbon-atom, in that it does not readily decompose into cinnamic acid and carbonic anhydride. Further, it readily takes up a molecule of water, with simultaneous decomposition into its two derived components, benzaldehyde and malonic acid. *Ethyl benzalmalonate*,  $\text{CHPh}:\text{C}(\text{COOEt})_2$ , is readily obtained from a mixture of ethyl malonate and benzaldehyde, either by passing hydrochloric acid to saturation, or by heating them in a sealed tube with acetic anhydride. It is a colourless tasteless viscous and strongly refractive liquid, sp. gr. = 1.115, and boils at  $215\text{--}217^\circ$  under a pressure of 30 mm.; it is readily saponified by baryta-water, yielding *benzalmalonic acid*,  $\text{CHPh}:\text{C}(\text{COOH})_2$ , which crystallises in short prisms melting at  $195^\circ$ , soluble in alcohol, insoluble in benzene and chloroform. By a protracted heating at its boiling point, it is gradually decomposed into cinnamic acid and carbonic anhydride. When boiled with water, it yields benzaldehyde and malonic acid, thus:



The salts of benzalmalonic acid are crystalline substances, more stable in the presence of water than their parent acid; the ferric, lead, mercuric, and cadmium salts are sparingly soluble precipitates. By nascent hydrogen, benzalmalonic acid is converted into benzylmalonic acid, thus:  $\text{CHPh}:\text{C}(\text{COOH})_2 + \text{H}_2 = \text{CH}_2\text{Ph}.\text{CH}(\text{COOH})_2$ . It does not, however, similarly take up a molecule of bromine, but is decomposed to form  $\alpha$ -bromocinnamic acid, in accordance with the equation—



A study of the reaction between benzaldehyde and the ethyl salt of ethylmalonic acid did not give satisfactory results.

It is remarked in a footnote that Culp has obtained from furfur-aldehyde and ethyl malonate a condensation-product, ethyl furfural-malonate, and its corresponding carboxylic acid. V. H. V.

**Action of Aldehydes on Ketones, Ketonic Acids, and Malonic Acid.** By L. CLAISEN (*Annalen*, 218, 121—128).—In this paper some general remarks are offered on the reactions obtained between the aldehydes and ketones or their derivatives. The results of Chiozza, Schmidt, and the author's researches on the action of benz- and furfur-aldehyde on acetaldehyde have established that only such methyl or methylene-groups as are directly combined with the carbonyl residue, exchange their hydrogen for the hydrocarbon residue of the aldehyde. In this respect the condensation between aldehydes and ketones resembles that between the aromatic aldehydes and fatty acids (Perkin's reaction); for in this case only the  $\text{CH}_2$  or  $\text{CH}$  residue attached to the carboxyl-groups enters into the reaction.

Further, either or both of the hydrocarbon residues attached to the carbonyl-group may take part in the condensation with formation of a mono- or a di-derivative. It seemed that a study of the action of aldehydes on malonic acid or its alkyl salts, as containing a methylene residue associated with two carbonyl-groups  $\text{CO}-\text{CH}_2-\text{CO}$ , would be a suitable extension of these general reactions. (The results of the experiments are detailed in the Abstracts, this vol., pp. 422, 443 and 444.) V. H. V.

**The Three Nitracetophenones.** By H. GEVEKOHT (*Annalen*, 221, 323—335).—That portion of the paper which relates to the preparation of the three nitracetophenones has already appeared in this Journal (Abstr., 1883, 191). *Orthamidoacetophenone*, obtained by reducing the nitro-compound with tin and hydrochloric acid, is identical with the amidoacetophenone which Baeyer and Bloem (Abstr., 1883, 197) prepared from orthamidophenylpropionic acid.

By the action of bromine on orthonitracetophenone dissolved in glacial acetic acid, mono- and di-bromo-derivatives are formed. The monobromo-derivative  $\text{C}_6\text{H}_4(\text{NO}_2).\text{CO}.\text{CH}_2\text{Br}$  crystallises in colourless needles melting at  $55^\circ$ , which have a bitter taste. The dibromo-compound forms crystalline prisms which melt at  $85^\circ$ . *Dichlororthonitracetophenone* crystallises in colourless plates, melting at  $73^\circ$ . Each of these three compounds is freely soluble in alcohol, ether, and chloroform. On reducing their alcoholic solutions by ammonium sulphide, indigo-blue is produced. Orthonitracetophenone is attacked by phosphorus pentachloride at the ordinary temperature, and is converted into orthonitromonochlorostyrene.

The ethylic salt of nitrobenzoylacetic acid is decomposed when boiled with dilute sulphuric acid, and yields a mixture of nitrobenzoic acid and *orthonitrobenzoylacetone*,  $\text{NO}_2.\text{C}_6\text{H}_4.\text{CO}.\text{CH}_2.\text{COMe}$ . Nitrobenzoylacetone forms yellow crystals melting at  $55^\circ$ , soluble in alcohol and ether. It combines with alkalis to form soluble salts of a yellow colour, and it also unites with phenylhydrazine, forming a crystalline compound melting at  $120^\circ$ , which probably has the constitution  $\text{NO}_2.\text{C}_6\text{H}_4.\text{C}(\text{N}_2\text{HPh}).\text{CH}_2.\text{C}(\text{N}_2\text{HPh}).\text{Me}$ . W. C. W.

**Transformation of the Fluobenzoic Acids in the Animal Organism.** By F. COPPOLA (*Gazzetta*, **13**, 521—525).—The experiments were made by giving to a middle-sized dog 5 grams of a fluobenzoic acid, in two doses daily, which did not affect him injuriously. The urine passed in the 48 hours was then evaporated to a syrup; this was treated with alcohol; the solution was filtered; and the residue left on distilling off the alcohol was decomposed with hydrochloric acid and digested with ether. On then distilling off the ether, there remained a strongly acid, oily mass, consisting of a fluohippuric acid, formed by combination of the fluobenzoic acid with the glycocine derived from the animal organism, and having the ortho-, meta-, or para-constitution according to the modification of fluobenzoic acid employed. The union was in all cases complete, no trace of free fluobenzoic acid being discovered in the urine.

The three fluohippuric acids,  $C_9H_8FNO_3$ , thus obtained are very similar in appearance, crystallising in radiate groups of needle-shaped prisms having a nacreous lustre. They are very soluble in ether, alcohol, and ethyl acetate, slightly soluble (the *p*-modification insoluble) in chloroform, insoluble in carbon bisulphide and in benzene. The *ortho*-modification melts at  $121.5^\circ$ , the *meta*- at  $152^\circ$ , and the *para*- at  $161$ — $161.5^\circ$ . They are decomposed by boiling with hydrochloric acid into glycine and the corresponding fluobenzoic acids.

H. W.

**New Synthesis of Cinnamic Acid.** By A. MICHAEL (*Amer. Chem. J.*, **5**, 205—206).—A satisfactory yield of cinnamic acid is obtained by heating malonic acid and benzaldehyde in molecular proportions in a sealed tube at  $140^\circ$  for several hours.

A. J. G.

**Dry Distillation of Parahydroxybenzoic Acid.** By A. KLEPL (*J. pr. Chem.*, **28**, 193—219).—Parahydroxybenzoic acid begins to decompose when heated above  $300^\circ$ , carbonic anhydride being evolved, whilst phenol and water distil over, and the acid becomes cloudy from separation of a white liquid which gradually collects at the bottom of the retort. When the temperature reaches  $350^\circ$ , the contents of the retort solidify, forming a yellowish-white amorphous mass, which closely resembles salicylide and glycollide, and which the author accordingly calls parahydroxybenzide.

*Parahydroxybenzide*,  $C_7H_4O_2$ , is obtained pure by repeatedly boiling the above-mentioned white residue with absolute alcohol. It is a white amorphous powder which does not dissolve in any of the ordinary solvents. It carbonises when heated above  $350^\circ$ . When boiled with potash, it is converted into parahydroxybenzoic acid. When heated on a water-bath with five times its weight of sulphuric acid, it yields *sulphoparahydroxybenzoic acid*, which crystallises from water in rhombic plates. The *barium salt*, which forms colourless prisms, loses 7 mols.  $H_2O$  when heated to  $120$ — $130^\circ$ . The *silver salt* is obtained by treating the barium salt with silver sulphate; it crystallises in irregular brown prisms containing no water of crystallisation. The formation of a very insoluble acid potassium salt is highly characteristic of the sulphonic acid. Extremely dilute solutions of the acid yield a precipitate on addition of sulphuric acid and

potash solution. The acid salt,  $C_7H_5SO_6K + H_2O$ , crystallises in quadratic prisms, or when formed in a very dilute solution, rectangular plates.

*Phenyl phenylparahydroxybenzoate*,  $OPh.C_6H_4.COOPh$ , is prepared by passing carbonic anhydride, heated to  $170-200^\circ$ , over parahydroxybenzide at  $400^\circ$ . After purification from absolute alcohol and glacial acetic acid, it crystallises in white scales which melt at  $73-78^\circ$ . When boiled with alcoholic potash or concentrated hydrochloric acid, it is decomposed into phenol and an acid of the composition  $C_{13}H_{10}O_3$ , which crystallises from chloroform in prisms melting at  $159.5^\circ$ . It forms a liquid ethyl salt. When the acid is distilled with baryta, the pure phenyl ether distils over as a colourless oily liquid, which solidifies in a freezing mixture, forming long needles melting at  $27-28^\circ$ . The compound,  $C_{13}H_{10}O_3$ , appears to be paraphenoxybenzoic acid,  $C_6H_4(OPh).COOH$ .

When parahydroxybenzide is distilled in a current of chlorine, a small quantity of an oil consisting of a mixture of chlorinated substances passes over, and in addition, long glittering needles melting at  $222^\circ$ , of a substance possessing all the characteristic properties of Julin's carbon chloride,  $C_6Cl_6$ .

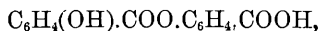
*Parahydroxybenzonitrile*,  $C_6H_4(OH).CN$ , is formed when parahydroxybenzide is heated at  $250^\circ$  in a current of ammonia gas. It crystallises in large rhombic plates melting at  $112-113^\circ$ . When boiled with potash, it yields ammonia and parahydroxybenzoic acid.

Parahydroxybenzide is converted into parahydroxybenzoic acid by the action of superheated steam at  $250^\circ$ .

*Parachlorobenzotrichloride*,  $C_6H_4Cl.CCl_3$ , is obtained by heating parahydroxybenzide with five times its weight of phosphorus pentachloride in a sealed tube at  $290-300^\circ$ . It boils at  $240-260^\circ$ . Concentrated sulphuric acid converts it into chlorosalicylic acid.

*Diparahydroxybenzoylparahydroxybenzoic Acid*. — The solid cake which is obtained by distilling parahydroxybenzoic acid contains, in addition to parahydroxybenzide, two parahydroxybenzoylparahydroxybenzoic acids. They may be regarded as being parahydroxybenzoic acid in which the hydrogen of the phenolic hydroxyl-group is replaced by the radical parahydroxybenzoyl. In the case of diparahydroxybenzoylparahydroxybenzoic acid the substitution is carried further, by the introduction of a second parahydroxybenzoyl-group in the phenol of the first. The latter acid forms a white powder melting at  $280^\circ$ , very sparingly soluble in alcohol and ether, insoluble in water and in chloroform. It dissolves freely in soda-solution, carbonate of soda, and ammonia.

*Parahydroxybenzoylparahydroxybenzoic acid*,



is best obtained by interrupting the distillation of parahydroxybenzoic acid when it has lost about 15 per cent. in weight. The residue is first treated with chloroform to remove resinous substances, then with water to dissolve undecomposed parahydroxybenzoic acid, and afterwards with 50 per cent. alcohol to dissolve the parahydroxybenzoylparahydroxybenzoic acid. The last crystallises in microscopic

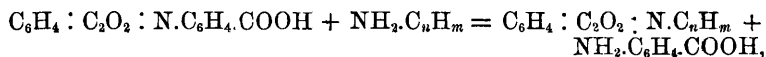
needles melting at 261°. It dissolves freely in alkalis; but such solutions quickly decompose, forming parahydroxybenzoic acid. It forms a sodium salt and two barium salts. When heated with acetic anhydride, it yields an acetyl-compound which crystallises in plates melting at 216.5°. The corresponding acetyl salt of diparahydroxybenzoylparahydroxybenzoic acid forms glittering plates melting at 185°. The author states that acids containing more parahydroxybenzoyl-groups appear to exist.

III. *Phenyl parahydroxybenzoate*,  $C_6H_4(OH).COOPh$ .—The distillate from parahydroxybenzoic acid contains, in addition to phenol, water and phenyl parahydroxybenzoate. It forms rhombic plates melting at 176°. It is insoluble in water. When treated with acetic anhydride it yields an acetyl-compound which crystallises in long plates melting at 84°.

J. I. W.

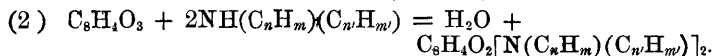
### Action of Phthalic Anhydride on Secondary Monamines.

By A. PIUTTI (*Gazzetta*, 13, 542—563).—The author has already shown (*Abstr.*, 1883, p. 999) that phthalamidobenzoic acid reacts with primary amines in the manner shown by the equation:—



whence it appears that this acid, so far as its phthalic component is concerned, behaves like phthalic anhydride, *i.e.*, it unites with the amine, forming the corresponding substituted phthalimide. The study of the action of phthalamidobenzoic acid on secondary monamines resolves itself therefore into that of the action of phthalic anhydride on the same bodies. The present paper describes the results obtained in this direction.

The action of phthalic anhydride on secondary monamines may be supposed to take place in two ways, yielding (1) a disubstituted phthalamic acid; and (2) a tetrasubstituted-derivative of a phthalic diamide:—



With the bases on which the author has experimented, *viz.*, ethylaniline, diphenylamine, piperidine, and conine, the action takes place in both these ways, the substituted phthalamic acid, as it forms, uniting with the base which has not yet entered into the reaction, and forming a salt, which, under the influence of heat, gives up a molecule of water, and yields a substituted diamide.

ACTION OF PHTHALIC ANHYDRIDE ON ETHYLANILINE.—The alkyl-derivatives of aniline prepared from commercial aniline, even after purification, cannot be separated from one another by fractional distillation, and moreover they frequently contain substituted ortho- and para-toluidines, together with unaltered toluidine and aniline. A sample of ethylaniline, after repeated fractional distillation, was



divided into two portions, boiling respectively at 203—209° and 209—215°; and in order to obtain pure compounds from these fractions, they were treated with  $\frac{1}{20}$  of the quantity of phthalic anhydride required to convert into an amide the entire quantity of ethylaniline present, supposing it to be pure. The liquid was then heated in a reflux apparatus; the first portion containing water was distilled off; and the last anhydrous distillate was again subjected to the action of  $\frac{1}{20}$  phthalic anhydride, and so on. Each time there was left in the flask a residue, often crystalline, from which the small remainder of free base not removed by distillation was separated by hydrochloric acid. The hard residue then left was washed with water, dried, and dissolved in alcohol, and the several compounds separated from the solution by fractional crystallisation. In this manner the following products were obtained:—

From the portion of the ethylaniline boiling at 203—209°, by the action of  $\frac{1}{20}$  phthalic anhydride:—

In the first treatment, *phenylphthalimide*, in the second, *phenylphthalimide* with a small quantity of *orthotolylphthalimide*; in the third, *o-tolylphthalimide* together with small quantities of *phenylphthalimide* and *ethylanilphthalein*; in the fourth, *o-tolylphthalimide* and *ethylanilphthalein*; in the fifth, sixth, and seventh, *ethylanilphthalein* and *ethyltoluidinephthalein*.

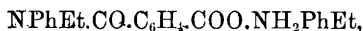
After the last treatment, the ethylaniline was separated by fractional distillation into two portions, one boiling at 204—205°, and consisting of nearly pure ethylaniline, while the other, which boiled at a higher temperature, consisted in great part of tertiary bases, and was therefore added to the following portion. This last portion of ethylaniline (209—215°) on treatment with  $\frac{1}{20}$  phthalic anhydride yielded *o-tolylphthalimide*, and in the second and third treatments, *ethyltoluidinephthalein*. After these treatments, there remained diethylaniline boiling at 213—215°, which gave only a slight turbidity with cœnanthal, and therefore contained only traces of secondary bases.

The author then proceeds to describe—first the products obtained by the action of phthalic anhydride on purified ethylaniline; then the substituted amides formed by treating the two portions of the mixed ethylanilines; and lastly orthotolylphthalimide.

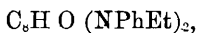
*Ethylphenylphthalamic acid*,  $C_{16}H_{16}NO_3 = NPhEt.CO.C_6H_4.COOH$ , is formed on dissolving 1 mol. phthalic anhydride in 2 mols. ethylaniline, and remains on exhausting the product with ether, and evaporating the solvent, as a colourless oil, heavier than water, somewhat soluble therein, very easily soluble in alcohol, ether, and other ordinary solvents. Hydrochloric acid decomposes it, yielding phthalic acid and ethylaniline hydrochloride. It unites with all the alkaline bases, forming salts moderately soluble in water. The *copper salt*,  $(C_{16}H_{14}NO_3)_2Cu$ , is precipitated on adding cupric acetate to a moderately concentrated solution of the ammonium salt, and when dried forms a light blue powder somewhat soluble in cold water, melting in boiling water, and solidifying on cooling to a green resin. A similar deportment is exhibited by all the insoluble or slightly soluble salts of this acid, and in general of all the substituted phthal-

anic acids hitherto examined. The copper salt begins to give off ethylaniline at about  $100^{\circ}$ , and at higher temperatures melts and decomposes, yielding ethylaniline and phenylphthalimide. The *barium salt*, obtained by neutralisation, is moderately soluble in water, more freely in alcohol, but does not crystallise. On adding silver nitrate to the ammonium salt the *silver salt* is precipitated in clots which blacken quickly on exposure to light.

*Ethylaniline Ethylphenylphthalamate*,



formed by direct combination, is uncrystallisable, and dries up in the exsiccator to a resinous mass which gradually becomes coloured. It is moderately soluble in alcohol, less in ether and in water, more soluble in cold than in hot water. Heated above  $200^{\circ}$ , it gives off 1 mol. water, and is converted into an amidated compound



which is not a derivative of the normal diamide of phthalic acid, but, as will presently be shown, must be regarded as a derivative of an unsymmetrical diamide, *i.e.*, as a phthalein of ethylaniline.

*Ethylanilphthalein*, prepared in the manner just mentioned, is obtained, after a few crystallisations from ether, in very fine prismatic shining crystals melting at about  $140^{\circ}$ . They are identical with the product obtained in the final treatment of the ethylanilines boiling at  $203$ — $209^{\circ}$  with phthalic anhydride. When this body is recrystallised from alcohol, it melts at  $140.5^{\circ}$  to  $141.5^{\circ}$ . It is insoluble in water, soluble in alcohol, especially when hot, also in ether and in benzene. The etheric solution yields it, on slow evaporation, in large crystals 2 cm. long, forming a characteristic twin-combination, and when isolated presenting the aspect of celestin. Ethylanilphthalein is insoluble in aqueous, but soluble in alcoholic potash, and does not decompose when boiled with that solvent, even for a long time. By fused potash, on the other hand, it is easily and completely resolved into ethylaniline and phthalic acid. It decomposes partially at  $300^{\circ}$ , but is reproduced and deposited in crystals on the cold sides of the containing vessel.

*Ethyltoluidine-phthalein*,  $\text{C}_8\text{H}_4\text{O}_2(\text{N.C}_2\text{H}_5\text{C}_7\text{H}_7)_2$ .—In the second and third treatments with phthalic acid of that portion of the mixed ethylanilines which boils at  $209$ — $215^{\circ}$ , and from the alcoholic mother-liquors of ethylanilphthalein formed by the action of phthalic anhydride on the portions boiling at  $203^{\circ}$  to  $209^{\circ}$ , there is obtained an uncrystallisable substance, transparent, somewhat coloured, melting at a low temperature, insoluble in hydrochloric acid and in strong potash-ley. After purification by repeated extraction with these solvents, and drying in the exsiccator at about  $90^{\circ}$ , it gave by analysis numbers agreeing with the formula of *ethyltoluidinephthalein*. It appears to be the phthalein of ethyl-orthotoluidine, inasmuch as metatoluidine is not found in commercial aniline, and the author on treating with phthalic anhydride the first portion of the mixed ethylanilines, found orthotolylphthalimide quite free from the para-compound.

*Diphenylphthalamic acid*,  $C_{20}H_{15}NO_3 = NPh_2.CO.C_6H_4.COOH$ , is formed by heating diphenylamine and phthalic anhydride in molecular proportions, the heat being gradually raised to  $250^\circ$  and kept at that point for about an hour. The product on cooling solidifies to a brown-green mass of diphenylamine diphenylphthalamate containing needles of phthalic anhydride. On dissolving this mass in a small quantity of hot alcohol and adding aqueous ammonia, the diphenylamine is precipitated, while ammonium diphenylphthalamate and phthalate remain in solution. This solution gives off ammonia during concentration and deposits yellow needles of diphenylphthalamic acid, additional quantities of which may be obtained from the mother-liquors. This acid, after several recrystallisations from alcohol, forms large white hard mammellated groups intermixed with small shining prisms. It melts at  $147^\circ$  to  $148^\circ$ , is insoluble in water, slightly soluble in ether, very freely in alcohol. It dissolves in alkalis, and is precipitated by strong acids; also in cold sulphuric acid, but the solution on addition of nitric acid does not give the reaction of diphenylamine. Its *silver salt*,  $C_{20}H_{14}NO_3Ag$ , crystallises in white nodules, quickly blackened by light. The *copper salt* is a light sky-blue powder. The *lead* and *barium salts* are insoluble in water.

*Diphenylamine diphenylphthalamate*, formed by fusing the acid and base together in molecular proportion, is a coloured solid mass which dissolves in ether, but does not crystallise therefrom. Heated for some time above  $300^\circ$ , it gradually loses water, turns dark brown, and is converted into the corresponding phthaleïn, viz.,

*Diphenylamine-phthaleïn*,  $C_{20}H_{14}N_2O_2 = (NPh_2)_2C < \underset{O}{\underset{|}{C}} > CO$ , which

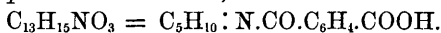
may also be prepared directly by boiling in a reflux apparatus for several hours, a mixture of 1 mol. phthalic acid and 2 mols. diphenylamine, as long as water is given off. The product is a solid highly coloured mass soluble in ether, benzene, and alcohol, especially when hot, and separating from the concentrated ethereal solution as a crust of transparent slightly coloured crystals. From alcohol, it crystallises in stellate groups of long, very white, shining needles melting at  $238-238.5^\circ$ . It is insoluble in aqueous potash, and is decomposed by very strong boiling or fused potash, into diphenylamine and phthalic acid. It dissolves in strong sulphuric acid, and on adding a drop of nitric acid, a splendid violet colour is developed, which disappears on addition of water, a brown substance being then deposited which redissolves in strong sulphuric acid with the coloration above mentioned. The solution of diphenylamine in sulphuric acid treated in the same manner gives, on the other hand, a deep blue coloration. Diphenylamine-phthaleïn is converted by strong nitric acid into a nitro-compound which dissolves in alcohol and crystallises therefrom in yellow leaflets, turning deep red on addition of ammonia. The potassium compound has a deep blood-red colour, but does not crystallise from alcoholic solution even highly concentrated.

The diphenylamine-phthaleïn prepared as above is identical with that which Lellman obtained (*Ber.*, 15, 830, and *Abstr.*, 1882, 1060) by the action of phthalyl chloride on diphenylamine; and, admitting

for this chloride the formula  $C_6H_4<\overset{CCl_2}{\underset{CO}{-}}>O$ , proposed by Ador and demonstrated by v. Gerichten (Abstr., 1880, 470—473), it follows that diphenylamine-phenylphthalein must be represented by the formula  $(NPh_2)_2C<\overset{C_6H_4}{\underset{O}{-}}>CO$ , the general formula of bodies of the same class being  $[N(C_nH_m)(C_mH_m)]_2 C<\overset{C_6H_4}{\underset{O}{-}}>CO$ .

When a solution of diphenylphthalamic acid in a slight excess of ethylaniline is boiled for some time, diphenylamine ethyl-phenyl-phthalamate is formed, which is resolved by hydrochloric acid into ethylphenylphthalamic acid and diphenylamine. On heating the same salt at a higher temperature, coloured products were formed, the composition of which could not be determined.

*Piperilene-phthalamic Acid,*

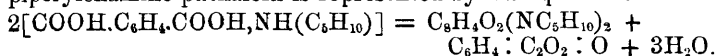


—On gradually adding phthalic anhydride to piperidine in a cooled vessel, a white crystalline mass is formed containing piperilene-phthalamic acid, partly free, partly combined with the piperidine; and on adding a small quantity of water and agitating with ether, the phthalic acid formed by the action of the water on the excess of the anhydride separates the piperilene-phthalamic acid from its piperidine salt, and the ether removes the whole of this acid from the aqueous solution. On evaporating the etheric solution, an oily residue is left consisting almost wholly of piperilene-phthalamic acid, while the water retains in solution the acid phthalate of piperidine which does not crystallise even when left for a long time over sulphuric acid.

Piperilene-phthalamic acid is a thick colourless oil, somewhat soluble in water, abundantly in alcohol. It forms soluble salts with the alkalis, and is reprecipitated from the solutions by the stronger acids. By the prolonged action of hydrochloric acid, it is resolved into piperidine and phthalic acid. Its *copper salt*,  $(C_{13}H_{14}NO_3)_2Cu$ , formed by double decomposition, is a light-blue precipitate.

The acid phthalate of piperidine which is obtained in the preceding reaction, together with piperilene-phthalamic acid, loses a molecule of water when heated, being thereby converted into piperilene-phthalamic acid:  $C_5H_{11}N.C_6H_4(COOH)_2 = H_2O + C_5H_{10}N.CO.C_6H_4.COOH$ .

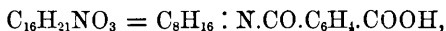
*Piperylenamine-phthalein*,  $C_8H_4O_2(NC_5H_{10})_2$ , is formed by heating the acid phthalate of piperidine at  $210^\circ$  as long as phthalic anhydride continues to sublime, treating the pasty and slightly coloured product with strong potash-lye, and cooling with ice: it then separates as a somewhat consistent mass, which may be purified from free phthalic acid by repetition of the treatment. On evaporating the etheric solution, the piperylenamine-phthalein remains as a nearly colourless oil, soluble in the ordinary solvents and in excess of cold aqueous potash, and partly precipitated from the last-mentioned solution on heating. The transformation of acid phthalate of piperidine into piperylenamine-phthalein is represented by the equation:



The compound thus prepared is identical with that obtained by R. Schiff (Abstr., 1880, 127) by the action of 2 mols. piperidine on 1 mol. phthalic anhydride in alcoholic solution, and regarded by him as phthalyl-piperide.

*Piperylenamine-phthaleïn dibromide*,  $C_8H_4O_2(NC_5H_{10})_2, Br_2$ , is formed on dropping a dilute etheric solution of bromine into an etheric solution of the phthaleïn, whereupon a red heavy oil is first formed which, as the addition of bromine is continued, crystallises completely in groups of shining prisms. It gave by analysis 33.3 per cent. bromine, the formula requiring 34.7 per cent.

*Conilene-phthalamic acid*,



is prepared from phthalic anhydride and conine in the same manner as the corresponding piperylene-compound, and crystallises in mammellated groups of colourless needles, which after recrystallisation from hydrochloric acid melt at  $155^\circ$ . By keeping, they become brown and opaque. The compound is but slightly soluble in ether and in water, somewhat more freely in benzene, easily in aqueous ammonia, from which it crystallises on addition of hydrochloric acid. Its ammonium salt does not precipitate barium chloride, but forms with lead acetate and silver nitrate white precipitates slightly soluble or insoluble in water. The *copper salt*,  $(C_{16}H_{20}NO_3)_2Cu$ , is a light-green powder slightly soluble in water.

*Conilenamine-phthaleïn*,  $C_8H_4O(NC_8H_{16})_2$ , is formed on heating the conilene-phthalamate of conine at a temperature above  $210^\circ$ . The product thus obtained is coloured, but may be purified by dissolving it in strong potash-lye, extracting with ether, washing with hydrochloric acid, again extracting with ether, and removing the hydrochloric acid from the etheric solution by agitation with dilute potash. On evaporating the ether, the conilenamine-phthaleïn remains as a thick nearly colourless oil, having a faint odour of conine. When quite dry, it forms an amorphous faintly fluorescent mass. It is moderately soluble in the ordinary solvents, and resists the action of hot strong potash-lye, but is resolved by fusion with potash into conine and phthalic acid. By treatment with bromine in etheric solution, it is converted into a red noncrystalline compound, which gradually gives off bromine, and appears to be analogous in composition to the compound similarly formed from piperylenamine-phthaleïn.

*Orthotolylphthalimide*,  $C_{15}H_{11}NO_2 = C_6H_4 : C_2O : N.C_6H_4Me$ , is obtained, together with phenylphthalimide, by the action of phthalic anhydride on the first portion of the mixed ethylanilines (p. 449) boiling at  $203-209^\circ$ , and separates in mammellated groups of nearly white crystals, melting at  $179^\circ$ , and more soluble in alcohol than phenylphthalimide. With potash, it reacts like other substituted phthalimides, yielding phthalic acid and a volatile base. H. W.

**Orthamidotolueneparathiosulphonic Acid.** By W. PAYSAN (*Annalen*, 221, 360—364).—*Orthamidotolueneparathiosulphonic acid*,  $C_7H_8(NH_2)SO_2.HS$ , resembles paramidotoluenearthiosulphonic acid in its properties and mode of preparation. It crystallises in four-

sided prisms, soluble in hot water; it decomposes at  $115^{\circ}$  without melting. The salts which this acid forms with the alkalis and alkaline earths are very soluble in water. The lead, silver, and copper salts are insoluble. Orthamidotolueneparasulphonic acid crystallises in large plates soluble in hot water. It decomposes at  $160^{\circ}$  without melting. The crystals of the barium salt,  $(\text{NH}_2\cdot\text{C}_7\text{H}_6\cdot\text{SO}_2)_2\text{Ba} + 2\text{H}_2\text{O}$ , and the anhydrous potassium salt are freely soluble; the crystalline silver salt and the amorphous lead salt are sparingly soluble in water. By decomposing the diazo-compound with alcohol, an ethoxytoluenesulphonic acid is obtained which appears to be identical with that described by Hayduck (*Annalen*, **172**, 215).

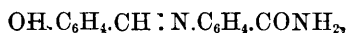
*Toluenesulphamine*,  $\text{C}_7\text{H}_6\text{SO}_2\text{H}\cdot\text{NH}_2$ , prepared by boiling the sulphonic acid with hydrochloric acid, is deposited from alcohol in needle-shaped crystals melting at  $175^{\circ}$ , soluble in ether. The hydrochloride,  $\text{C}_7\text{H}_6\text{SO}_2\text{H}\cdot\text{NH}_2\cdot\text{HCl}$ , crystallises in slender needles, soluble in water. It decomposes at  $100^{\circ}$  without melting. W. C. W.

**Paramidotoluene-orthothiosulphonic Acid.** By A. HEFFTER (*Annalen*, **221**, 345—359).—Paranitrotoluene-orthosulphonic chloride is added to a well-cooled solution of ammonium sulphide. After removing the precipitated sulphur by filtration, acetic acid is added, when the *amidotoluenethiosulphonic acid*,  $\text{C}_7\text{H}_6(\text{NH}_2)\cdot\text{SO}_2\cdot\text{SH}$ , is deposited. This acid forms yellow prisms, which are sparingly soluble in water, and insoluble in alcohol and ether. It is decomposed by acids at the ordinary temperature, and also by boiling with water. The barium,  $(\text{NH}_2\cdot\text{C}_7\text{H}_6\cdot\text{SO}_2\cdot\text{S})_2\text{Ba} + 2\text{H}_2\text{O}$ , mercuric, and copper salts are crystalline; the silver and lead salts are amorphous. Sodium-amalgam converts the thiosulphonic acid into *paramidotoluene-orthosulphonic acid*,  $\text{NH}_2\cdot\text{C}_7\text{H}_6\cdot\text{SO}_2\text{H}$ , which crystallises in colourless needles or prisms soluble in hot water. The salts of this acid are freely soluble in alcohol and water. The potassium salt crystallises in prisms, and the barium salt in needles, which are very deliquescent. Bromine-water converts the sulphonic acid into amidotoluenesulphonic acid and toluenesulphamine. By the action of nitrous acid on an alcoholic solution of amidotoluene-sulphonic acid, the diazo-compound is obtained, but if the acid is dissolved in hydrobromic acid instead of alcohol, Jenfsen's parabromotoluene-orthosulphonic acid (*Annalen*, **172**, 230) is produced. The diazo-compound crystallises in yellowish-brown needles. It is decomposed by alcohol, forming *ethoxytoluenesulphonic acid*,  $\text{EtO}\cdot\text{C}_7\text{H}_6\cdot\text{SO}_3\text{H}$ , which bears a close resemblance to the isomeride which Hayduck (*Annalen*, **172**, 215) obtained from the diazo-compound of orthamidotolueneparasulphonic acid. The barium salt,  $(\text{OEt}\cdot\text{C}_7\text{H}_6\cdot\text{SO}_3)_2\text{Ba} + 3\frac{1}{2}\text{H}_2\text{O}$ , forms glistening plates, soluble in alcohol and water. The potassium salt is deposited from alcoholic solutions in yellow plates. The chloride is a thick yellow oil, and the amide,  $\text{OEt}\cdot\text{C}_7\text{H}_6\cdot\text{SO}_2\text{NH}_2$ , forms white needles melting at  $136^{\circ}$ , and dissolving freely in alcohol, ether, and hot water. *Methoxytoluenesulphonic acid*,  $\text{MeO}\cdot\text{C}_7\text{H}_6\cdot\text{SO}_3\text{H}$ , yields very soluble potassium and barium salts, which crystallise with difficulty. The chloride is an oily liquid. The amide crystallises in prisms which melt at  $150^{\circ}$ .

Strong acids convert amidotoluenesulphonic acid into a base which

the author calls *toluenesulphamine*,  $C_7H_6SO_2H.NH_2$ . The base melts at  $132^\circ$ , and dissolves readily in alcohol and ether. It unites with acids to form a series of crystalline salts, *e.g.*,  $C_7H_6SO_2H.NH_2.HCl$ . Toluenesulphamine is converted into amidotoluenethiosulphonic acid by yellow ammonium sulphide, and into the sulphinic acid by the action of sodium-amalgam. W. C. W.

**Metamidobenzamide.** By H. SCHIFF (*Annalen*, **218**, 185—194).—The difference in chemical function of the two amido-groups in amidobenzamide,  $NH_2.C_6H_4.CO_2NH_2$ , is shown most markedly in its reaction with aldehydes, for the amido-group in the benzene nucleus combines with the hydrocarbon residue of the aldehyde far more readily than does the acid amido-group. For example, acetaldehyde and metamidobenzamide react in accordance with the equation  $Me.CHO + 2NH_2.C_6H_4.CONH_2 = CHMe(NH.C_6H_4.CONH_2)_2$ . The resultant substance is an amorphous powder, turning gold-coloured and finally red on exposure to air. When heated in sealed tubes at  $100$ — $120^\circ$  a further separation of water takes place, the aldehydic residue being introduced into the acid amido-group. Similarly on mixing aqueous solutions of salicylaldehyde and metamidobenzamide, glistening golden needles of *orthohydroxybenzyleneamidobenzamide*,



separate out. This compound melts at  $186^\circ$ , and is readily soluble in hot water and alcohol. By prolonged boiling with water, it is decomposed into its components, salicylaldehyde and metamidobenzamide. When the salicyl-derivative is heated with benzaldehyde, a further substitution-product is formed,



a crystalline substance which cannot be melted without decomposition. Its diacetyl-derivative crystallises in small needles, and decomposes at  $220^\circ$  with partial liquefaction.

A glucoside of the above monosalicyl-derivative of metamidobenzamide can be prepared by dissolving in warm water metamidobenzamide and helicine (glucosalicylaldehyde). It crystallises in colourless crystals melting at  $113^\circ$  to form a golden glass. Its composition is expressible by a formula—

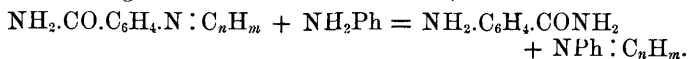


On warming with dilute hydrochloric acid, it is decomposed into salicylaldehyde, metamidobenzamide, and glucose.

Again metamidobenzamide combines with isatin, producing a compound, *isatomidobenzamide*,  $NH_2.CO.C_6H_4.N : C<\overset{C_6H_4}{\underset{CO}{-}}>NH$ , forming large golden crystals, which begin to melt at  $280$ , turning brown and evolving gas.

If the aldehyde- or helicin-derivatives of amidobenzamide be

warmed with aniline, the aldehydic grouping combines with the aniline, with regeneration of amidobenzamide, thus—



Similarly phthalamidobenzamide with aniline forms phenylphthalimide.

V. H. V.

**Oxidation of Substitution-products of Aromatic Hydrocarbons. XV.—Oxidation of  $\beta$ -Cymenesulphonamide.** By I. REMSEN and W. C. DAY (*Amer. Chem. J.*, 5, 149–161).—In this series of researches it has already been shown in the oxidation of paradiethylbenzenesulphonamide, [Et : SO<sub>2</sub>NH<sub>2</sub> : Et = 1 : 2 : 4], and of  $\alpha$ -cymenesulphonamide, [Me : SO<sub>2</sub>NH<sub>2</sub> : Pr<sup>a</sup> = 1 : 2 : 4], that the sulphonamide-group exerts a protecting influence on that hydrocarbon-group which occupies the ortho-position relatively to it. To ascertain the general nature of the rule, the authors now investigate the oxidation of  $\beta$ -cymenesulphonamide, [Pr : SO<sub>2</sub>NH<sub>2</sub> : Me = 1 : 2 : 4], and find that the propyl-group is protected and the methyl-group oxidised.

*Monobromocymene*, [Me : Br : Pr<sup>a</sup> = 1 : 2 : 4], is converted into the *sulphonic acid* by treatment with a mixture of ordinary and fuming sulphuric acids; the liquid solidifies on cooling to a mass of dark purple crystals; these are dissolved in water, the solution neutralised with chalk, and the resulting calcium salt obtained on evaporation in long needles of the formula (C<sub>10</sub>H<sub>12</sub>Br.SO<sub>3</sub>)<sub>2</sub>Ca + 9½H<sub>2</sub>O. The barium salt, (C<sub>10</sub>H<sub>12</sub>Br.SO<sub>3</sub>)<sub>2</sub>Ba + 9½H<sub>2</sub>O, the zinc salt, (C<sub>10</sub>H<sub>12</sub>Br.SO<sub>3</sub>)<sub>2</sub>Zn + 8H<sub>2</sub>O, and the magnesium salt, (C<sub>10</sub>H<sub>12</sub>Br.SO<sub>3</sub>)<sub>2</sub>Mg + 9½H<sub>2</sub>O, all crystallise in long needles. The sodium salt, C<sub>10</sub>H<sub>12</sub>Br.SO<sub>3</sub>Na + 4½H<sub>2</sub>O, crystallises in slender needles. *Bromocymenesulphonamide*, C<sub>10</sub>H<sub>12</sub>Br<sub>2</sub>.SO<sub>2</sub>NH<sub>2</sub>, crystallises in slender needles, melts at 197° (corr.), and is sparingly soluble in hot water, but readily in alcohol.

*$\beta$ -Cymenesulphonamide*, C<sub>10</sub>H<sub>13</sub>.SO<sub>2</sub>NH<sub>2</sub>, is prepared by treating a solution of sodium bromocymenesulphonate with sodium-amalgam until all the bromine is removed, the alkaline solution then being neutralised with sulphuric acid, the sodium sulphate crystallised out as far as possible, the mother-liquor evaporated to dryness, heated for some time at 110°, then treated with an equal weight of phosphorus pentachloride, the mixture being gently heated to complete the reaction. After cooling, the mass is treated with aqueous ammonia, and the mixture allowed to stand for 12 hours, when the sulphonamide separates in great part. After purification,  $\beta$ -cymenesulphonamide crystallises in glistening scales, melts at 151° (corr.), is insoluble in cold, sparingly soluble in hot water, readily soluble in hot alcohol. (Although from its method of formation this substance should have the constitution [Pr<sup>a</sup> : SO<sub>2</sub>NH<sub>2</sub> : Me = 1 : 2 : 4], yet the results obtained by the oxidation of paradipropylbenzenesulphonamide seem to throw some doubt on its really possessing that constitution. See next Abstract.) On fusion with potash, a strong odour of thymol was perceptible, but as the quantity of material employed was small, thymol could not be isolated from the product of the reaction. On oxidation with chromic mixture, it yields an acid of the formula C<sub>10</sub>H<sub>13</sub>O<sub>4</sub>SN, *sulphamineparapropylbenzoic acid*, C<sub>6</sub>H<sub>3</sub>Pr(SO<sub>2</sub>NH<sub>2</sub>)COOH [1 : 2 : 4],



which melts at  $244^{\circ}$  (corr.), and crystallises in long needles. The barium salt crystallises with  $2\frac{1}{2}\text{H}_2\text{O}$ , and is very soluble in water. The result of the oxidation confirms the rule that the sulphonamide group protects that hydrocarbon group occupying the ortho-position relatively to it.

A. J. G.

**Oxidation of Substitution-derivatives of Aromatic Hydrocarbons. XVI.—Oxidation of Paradipropylsulphonamide.** By I. REMSEN and E. H. KEISER (*Amer. Chem. J.*, 5, 161—171).—Paradipropylbenzene, prepared according to Körner's directions, is dissolved in fuming sulphuric acid, gently heated on the water-bath to complete the reaction, the liquid then being diluted and neutralised with barium carbonate. On evaporation, barium paradipropylbenzenesulphonate,  $(\text{C}_{12}\text{H}_{17}\cdot\text{SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$ , crystallises out in minute needles, which effloresce on exposure to air. The potassium salt,  $\text{C}_{12}\text{H}_{17}\cdot\text{SO}_3\text{K} + 4\text{H}_2\text{O}$ , crystallises in large transparent plates. By successive treatment with phosphorus pentachloride and ammonia, the potassium salt is converted into *paradipropylbenzenesulphonamide*,  $\text{C}_{12}\text{H}_{17}\cdot\text{SO}_2\text{NH}_2$ . This crystallises in rhombohedrons having the axial ratios  $a : c = 1 : 0.85592$ ; it melts at  $103^{\circ}$ , is sparingly soluble in boiling water, but readily in alcohol. On oxidation with chromic mixture, it yields a small quantity of sulphoterephthalic acid and a sulphamine-propylbenzoic acid,  $\text{C}_{10}\text{H}_{13}\text{SO}_4\text{N}$ , crystallising in long lustrous needles, and melting at  $212\text{—}213^{\circ}$  (corr.). The barium salt is not crystalline, the calcium salt,  $(\text{C}_{10}\text{H}_{12}\text{SO}_4\text{N})_2\text{Ca} + 6\text{H}_2\text{O}$ , does not crystallise well; a hydrogen copper salt,  $(\text{C}_{10}\text{H}_{12}\text{SO}_4\text{N})_2\text{Cu} = \text{C}_{10}\text{H}_{13}\text{SO}_4\text{N} + 2\text{H}_2\text{O}$ , is obtained in minute blue crystals by boiling the acid with copper oxide; the silver salt,  $\text{C}_{10}\text{H}_{12}\text{SO}_4\text{NAg}$ , is non-crystalline. Being derived from paradipropylbenzene, the acid must have the constitution  $\text{C}_6\text{H}_3\text{Pr}^a(\text{SO}_2\text{NH}_2)\cdot\text{COOH}$  [ $\text{Pr}^a : \text{SO}_2\text{NH}_2 : \text{COOH} = 1 : 2 : 4$ ]. The acid obtained by the oxidation of  $\beta$ -cymenesulphonamide (see preceding Abstract) should be identical with this, but the differences in the melting points of the acids and in the properties of their barium salts show that the acids are isomeric. Pending further investigation, the authors suggest the probability that during some of the operations employed in the preparation of  $\beta$ -cymenesulphonamide, the normal propyl-group must have undergone transformation into the isopropyl-group, a transformation of which many instances have been noted recently.

A. J. G.

**Decolorising Action of Ferric Salts on Indigo.** By L. MARGARY (*Gazzetta*, 13, 374—375).—In experiments on certain iron mordants for silk containing ferric sulphate and nitric acid, it was necessary to determine the amount of nitric acid present. This was done by means of indigo solution, and the author observed that the results were invariably too high. This he attributed to the oxidising action of the ferric salt, and found on heating the indigo solution with pure ferric sulphate that it was rapidly and completely decolorised, the ferric being reduced to a ferrous salt.

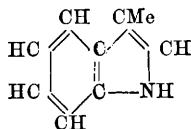
C. E. G.

**Transformation of Scatole into Indole, and Preparation of Indole.** By M. FILETI (*Gazzetta*, **13**, 378—381).—The author found that the vapour of scatole is decomposed when passed through a red-hot tube, a combustible gas being given off, whilst indole is found in the distillate. On this reaction he finds a new and advantageous method for preparing indole. If the vapour of cumidine, prepared by the distillation of barium amidocumate with excess of baryta, be passed over oxide of lead at a red heat, gas is evolved in abundance, and a black liquid condenses in the receiver, consisting of indole mixed with some unaltered cumidine and resinous substances. The product is first treated with hydrochloric acid to remove cumidine, distilled in a current of steam, the distillate acidified with hydrochloric acid, and the indole precipitated with picric acid. The precipitate, after being dried and washed with light petroleum, is distilled with ammonia, when the indole passes over with the aqueous vapour, and forms oily drops, which soon solidify; that which remains dissolved in the aqueous distillate may be extracted by agitation with ether and purified by crystallisation from water. It is necessary carefully to regulate the temperature of the lead oxide in order to obtain good results: if the temperature is too high, most of the material is carbonised; if too low, the cumidine passes over unchanged. In a successful operation cumidine gives 24 per cent. of its weight of the crude picrate. The gas given off contains ethane, ethylene, and propylene. This method of formation is interesting, as it confirms the author's opinion that indole is methyl scatole (see next Abstract), and is moreover the best method for preparing indole. C. E. G.

**Synthesis of Scatole.** By M. FILETI (*Gazzetta*, **13**, 358—363).—When barium nitrocumate is distilled with barium hydroxide and zinc powder—or better metallic iron—a dark coloured distillate is obtained of disagreeable odour, consisting of cumidine, scatole, and resinous substances: the yield of crude scatole picrate obtained when iron is used is about 10 per cent. A better result is obtained by reducing a portion of the nitrocumic acid (4 parts) to amidocumic acid, mixing it with the rest of the nitrocumic acid (6), and excess of crystallised barium hydroxide (10), drying at 120°, mixing it with twice its weight of dry barium hydroxide, and distilling in small portions of 50 grams at a time. Although the reaction is more regular than when the nitro-acid is used alone, care must be taken or the result will be unsatisfactory. The distillate is treated with dilute hydrochloric acid to remove cumidine, and then distilled in a current of steam, when some of the scatole collects in the condenser in snow-white plates, and the remainder may be recovered from the distillate by acidifying it with hydrochloric acid and precipitating with picric acid. After purifying the picric acid compound by crystallisation from benzene, it is decomposed with ammonia.

It would seem that in this reaction traces of indole are formed, but no methylketole. In reference to Baeyer's statement (*Ber.*, **13**, 2340) that pure scatole gives no coloration with fir wood moistened with hydrochloric acid, the author has been unable by any method of purification to obtain scatole which does not give this coloration. When

pure it has no fæcal odour, but a characteristic one recalling that of naphthylamine. Considering its mode of formation, its constitution may be graphically expressed as—



(See preceding Abstract.)

C. E. G.

**Oil of Hops obtained from Commercial Lupulin.** By J. OSSIPOFF (*J. pr. Chem.* [2], **28**, 447—448).—Personne found oil of hops to consist of a hydrocarbon,  $C_{10}H_{16}$ , and an oxygenated compound,  $C_{10}H_{16}O$ . The first is possibly a terpene, but the nature of the second is unknown. The author has undertaken the study of these substances, and in this preliminary notice he states that bromine, sulphuric acid, chromic acid, and sodium act on the purified oil.

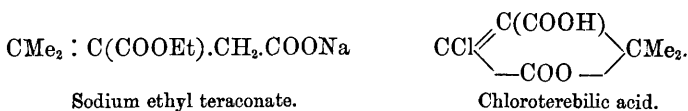
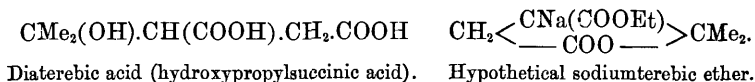
A. B.

**Oil of Birch.** By H. P. PETTIGREW (*Pharm. J. Trans.* [3], **14**, 167—168).—A thorough chemical investigation of the composition of this volatile oil has never been made, although Procter found that it contained salicylic acid and had similar properties to the oil of gaultheria; whilst Kennedy quite recently confirmed this result, and thus supported the presumed identity of the oil of birch with the oil of gaultheria. The author has now examined a perfectly pure sample of oil of birch, sp. gr. 1.180 at 15°, boiling point 218°, and finds that it consists of methyl salicylate only, and therefore differs from oil of gaultheria, which contains a terpene, and has a sp. gr. = 1.0318 at 22°, and not 1.180 as given in the United States Pharmacopœia.

D. A. L.

**Terebic Acid.** By W. ROSER (*Annalen*, **220**, 254—271).—A great part of this paper has already appeared (*Abstr.*, 1882, 716). *Sodium ethyl teraconate* crystallises in small white hygroscopic needles of the formula  $C_9H_{13}O_4Na$ . With silver nitrate this salt gives a crystalline silver salt; with copper acetate, a bluish-green amorphous precipitate. Mineral acids separate *hydrogen ethyl teraconate*,  $C_9H_{14}O_4$ , an acid liquid, slightly soluble in water. Its solutions decompose carbonates. It is easily saponified to teraconic acid, identical with that obtained by Geissler. On distilling terebic acid, partial decomposition ensues, carbonic acid is evolved, and a neutral body produced, which distils in a current of steam, and has the properties of a lactone. Terebic acid boiled with a large excess of potash yields potassium diaterebilate,  $C_7H_8O_5K_2$ , but the latter, when in a neutral solution, is very unstable, becoming alkaline on warming by the reformation of potassium terebilate,  $C_7H_7O_4K$ . A solution of  $\alpha$ -chloroterebic acid boiled with calcium or alkaline carbonates yields salts of hydroxyterebic acid. *Calcium hydroxyterebate*,  $(C_7H_9O_5)_2Ca$ , crystallises in microscopic tables; the *silver* salt forms easily soluble needles. The free acid was not obtained in a pure

state, but fuses above  $100^{\circ}$ . From the mother-liquors obtained in the preparation of  $\alpha$ -chloroterebic acid, another acid was isolated which appeared to be isomeric with the latter acid.  $\alpha$ -Chloroterebic acid, treated with phosphoric pentachloride at  $130$ – $140^{\circ}$ , yields *chloroterebic acid*,  $C_7H_7ClO_4$ , which is easily soluble in water, and crystallises in small prisms melting at  $200$ – $203^{\circ}$ . It is much more stable than  $\alpha$ -chloroterebic acid, and is not decomposed by boiling with water or silver oxide. Its *calcium* salt,  $(C_7H_6ClO_4)_2Ca + H_2O$ , crystallises in tables or prisms, and loses its water at  $170^{\circ}$ . The *silver* salt crystallises from water in long needles. Chloroterebic acid could not be obtained by the action of phosphoric chloride on terebic acid. The author gives the following formulæ as most probably correct:—



L. T. T.

**Thapsia Resin.** By F. CANZONERI (*Gazzetta*, 13, 514–521).—The root of *Thapsia Garganica*, a plant known for its vesicating properties, yields to boiling alcohol a white amorphous waxy substance, slightly soluble in ether and carbon bisulphide, and melting, after purification, at  $90^{\circ}$ . This substance however forms but a small part of the thapsia root. More abundant and important constituents are obtained by treating the dried and chopped root in a percolator with ether, whereby a yellow solution is obtained, which, on distilling off the ether, yields an amber-coloured syrupy resin possessing strong vesicating properties. This acid dissolves in strong aqueous potash at ordinary temperatures and in dilute potash when heated—in both cases with great rise of temperature,—and on neutralising the resulting solution with hydrochloric acid, a yellow curdy precipitate is formed, having an unpleasant odour, and consisting of a mixture of liquid and solid ethers and fatty acids, together with resinous substances. From this mixture of products, the author has obtained: (1.) An octoic or caprylic acid,  $C_8H_{16}O_2$ . (2.) A new acid of the series  $C_nH_{2n-2}O_4$ , which he designates as thapsic acid. (3.) A non-azotised neutral vesicating substance.

This last constituent was obtained in very small quantity only, and in some preparations was altogether absent; it is moreover very difficult to purify from resinous substances and wax, by which it is generally accompanied. It dissolves in hot alcohol, and separates on cooling in shining needles melting at  $87^{\circ}$ ; also in ether and in carbon bisulphide; all its solutions possess vesicating properties. Heated with strong potash-lye, it dissolves partially and is precipitated in the crystalline state on diluting the solution with water. It is not altered

by boiling with strong acids. Heated on platinum foil, it burns away without residue, emitting a pleasant odour.

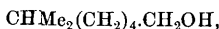
THAPSIC ACID,  $C_{16}H_{30}O_4$ , is obtained by pressing between paper the curdy precipitate formed on adding hydrochloric acid to the solution of the resin in aqueous potash, and crystallising it several times from boiling alcohol with addition of animal charcoal. It forms white shining scales melting at  $123-124^\circ$ , nearly insoluble in water, benzene, and carbon bisulphide, soluble in alcohol, less soluble in ether. When strongly heated, it distils without alteration; ignited on platinum foil, it burns with an odour of burnt wax. It is but slowly attacked by bromine or by strong nitric acid. It is a bibasic acid. Its *potassium salt*,  $C_{16}H_{28}O_4K_2$ , forms shining anhydrous prisms. The *barium salt*,  $C_{16}H_{28}O_4Ba$ , obtained by precipitation from the potassium salt, is a white amorphous powder insoluble in water and very slightly soluble in boiling alcohol. The *silver salt*,  $C_{16}H_{28}O_4Ag_2$ , is a white insoluble precipitate which blackens when heated or exposed to light.

Thapsic acid dissolves at boiling heat in aqueous ammonia, and the solution on cooling deposits a crystalline substance probably consisting of the corresponding amide. The acid heated with aniline at  $170-180^\circ$  in sealed tubes, is converted into the anilide,  $C_{16}H_{28}O_2(NHPh)_2$ , which forms a white crystalline powder melting at  $162-163^\circ$ , and acquiring a faint violet colour when exposed to the air.

The barium salt of thapsic acid distilled at a moderate heat with excess of barium hydroxide, yields a small quantity of hydrocarbons, saturated and non-saturated, having a musky odour, combining for the greater part with bromine, and forming a solid body which when dried between bibulous paper and crystallised from alcohol, forms white needles melting at  $73^\circ$ .

OCTOIC or CAPRYLIC ACID,  $C_8H_{16}O_2$ .—On distilling with steam the oily precipitate obtained by neutralising with hydrochloric acid the potash-solution of the ethereal extract of the resin, after removal of potassium thapsate and dilution with water, there passes over a yellow transparent oil, lighter than water. On exhausting this oil with ether, drying the etheric solution with calcium chloride and distilling, the greater part goes over at  $220-236^\circ$ ; and on fractioning this portion at intervals of  $5-5^\circ$ , three other fractions are obtained, the most abundant of which is a colourless liquid soluble in alcohol and ether, and solidifying when cooled with snow, in flexible laminae melting at ordinary temperatures. The product thus obtained is shown by analysis to have the composition of an octoic acid, and in its melting and boiling points it agrees nearly with the octoic acid obtained by saponification of cocoanut oil, and by oxidation of the octyl alcohol from heracleum oil, melting at  $16^\circ$ , boiling at  $236-237^\circ$ , which agreement the author has further confirmed by examination of the sodium, barium, and zinc salts.\*

\* The author, in accordance with the view hitherto generally entertained, regards this acid as normal octoic acid  $CH_3(CH_2)_6COOH$ , but recent investigations have shown that the primary octyl alcohol of heracleum oil is an iso-alcohol,



and consequently that the acid obtained from it by oxidation must be an iso-acid,  $CHMe_2(CH_2)_4\cdot COOH$ . (See Watts's *Dictionary of Chemistry*, 8, 379.)—H. W.

The author suggests that thapsic acid may be a *dioctioic acid*,  $C_8H_{15}O_2 \cdot C_8H_{15}O_2 = 2C_8H_{16}O_2 - H_2$ , formed from the octoic acid by slow oxidation in the body of the plant.

H. W.

**Red Resins known as Dragon's Blood.** By J. J. DOBBIE and G. G. HENDERSON (*Pharm. J. Trans.* [3], 14, 361—364).—Besides the red resins from *Pterocarpus Draco* and *Croton Draco*, there are three different recognised kinds of dragon's blood, one from the East Indies, *Calamus Draco*; one from Socotra, and one from the Canary Islands, *Dracaena Draco*. The first of these is the only one that has been fully described, but the results are not concordant; this is due apparently to the researches having been carried out on different substances. The authors have now investigated this subject, and have examined several varieties of the so-called dragon's blood, which they find can be arranged in four distinct groups: 1. Those which dissolve completely in chloroform, carbon bisulphide, and benzene; 2. Those soluble in chloroform, but insoluble in carbon bisulphide and benzene; 3. Those soluble in chloroform and benzene, and partly in carbon bisulphide; and 4. Those which are insoluble in all three reagents. The accuracy of this classification is supported by the physical properties of the resins and their behaviour towards reagents, and it is evident therefore that there were four different kinds of resins under examination. All the resins dissolve to a small extent in boiling water, those of Class 4 being rather more soluble than the others; they are all freely soluble in alcohol, ether, oil of cloves, and glacial acetic acid, leaving a variable amount of insoluble matter, which usually consists of vegetable tissue, sand, &c. They are all slightly soluble also in hydrochloric acid, those of Class 2 being the most soluble; ammonia reprecipitates them from this solution. The aqueous and alcoholic solutions have an acid reaction. When treated with sodium hydroxide, the resins effervesce and emit an odour like that of rhubarb. Ammonia forms a clear mixture with the alcoholic solutions. The resins were carefully purified by means of ether, and then powdered; the results of the individual class examinations may be thus summed up: Resin 1, brick-red, melting at about  $80^\circ$ , when decomposed by heat gives off very irritating red fumes. It dissolves readily with an orange-red colour in alcohol, ether, chloroform, carbon bisulphide, and benzene, but with difficulty in boiling caustic soda, ammonia, sodium carbonate, and with great difficulty in lime-water, whilst, in the cold, it is scarcely soluble in the first two and insoluble in the last two of the latter reagents. The ammonia solution is reddish-yellow, and a portion of the resin is not dissolved. The alcoholic solution gives a brown-red precipitate with lead acetate. Analysis (combustion and lead estimation) suggests the formula  $C_{18}H_{18}O_4$ . This variety is derived from *Calamus Draco*. Resin 2,  $C_{17}H_{19}O_6$ , origin uncertain, is carmine-red, melting at about  $100^\circ$ ; when heated it gives off non-irritating fumes. It dissolves freely in alcohol, ether, and chloroform with a pink colour, and in cold caustic soda, ammonia, sodium carbonate, and lime-water with purple colour changing to orange-red or yellow on boiling, whilst it is insoluble in carbon bisulphide and benzene. The alcoholic solution gives a lilac-coloured pre-

precipitate with lead acetate. Resin 3,  $C_{18}H_{18}O_4$ , from *Dracaena*, is vermilion, melting at about  $80^\circ$ ; when heated it evolves aromatic irritating red fumes. It dissolves with a blood-red colour in alcohol and ether, and in cold caustic soda, ammonia, lime-water, and sodium carbonate, but is insoluble in chloroform, carbon bisulphide, and benzene. Its alcoholic solution gives a mauve-coloured precipitate with lead acetate. Resin 4, is a mixture of a reddish-brown resin, freely soluble in carbon bisulphide, and a light brick-red resin, nearly insoluble in that menstruum. The two portions differ considerably with regard to their solubility in ether, benzene, and other reagents, the dark portion being the less soluble of the two. Cinnamic acid was detected in the first and third varieties (comp. Abstr., 1882, 209), but not in the others. Johnstone found two resins in one kind of dragon's blood, to the one he gave the formula,  $C_{20}H_{24}O_4$ , and to the other,  $C_{20}H_{21}O_4$ . D. A. L.

**Saponin.** By E. STÜTZ (*Annalen*, 218, 231—256).—At the commencement of this paper, an historical account is given of saponin, a drug obtained from the *Saponaria rubra* and its allied species. The formulæ proposed for this substance, deduced from the percentage proportions of carbon and hydrogen found in it, are various, but most experimenters are agreed in proving that it is decomposed on boiling with acids, yielding a carbohydrate among other products.

The source of the saponine studied in this paper was the bark of the *Quilbaja saponaria*, a member of the Spireæa family, indigenous in Chili and Peru. This was digested with water, the extract evaporated down, and hot alcohol of 90 per cent. added; on cooling, white flocks of saponin separated, which were then frequently recrystallised from alcohol, and finally purified by animal charcoal.

Saponin thus obtained is a white, amorphous, neutral powder, generally possessing an astringent taste, due to traces of impurities; it is soluble in water, insoluble in absolute alcohol and ether; its aqueous solution forms a lather like soap. When heated to  $195^\circ$  it turns brown, and at a higher temperature evolves a vapour resembling caramel in odour.

The author was unable to obtain saponin free from inorganic impurities; and from the properties of its barium compound it would appear probable that the impurities, principally consisting of calcium, were intimately associated with the saponin. From the mean of four concordant analyses the formula  $C_{19}H_{30}O_{10}$  is deduced.

A concentrated aqueous solution of saponin is precipitated by baryta-water; a substance of composition  $2C_{19}H_{30}O_{10} + Ba(OH)_2$  being formed, from which the barium is not readily separated by carbonic anhydride. In order to determine the number of alcoholic hydroxyl-groupings present in saponin, it was heated with acetic or butyric anhydride under various conditions. A series of acetyl-derivatives was thus obtained; amongst which are enumerated a tetracetyl,  $C_{19}H_{26}\overline{Ac}_4O_{10}$ , and a pentacetyl,  $C_{19}H_{25}\overline{Ac}_5O_{10}$ , derivative, and two compounds formed by the addition of acetic anhydride to the latter substance, viz.,  $C_{19}H_{25}\overline{Ac}_5O_9(O\overline{Ac})_2$ , and  $C_{19}H_{25}\overline{Ac}_5O_8(O\overline{Ac})_4$ . From these results it follows that the saponine contains five hydroxyl-

groups, and two oxygen-atoms combined only with carbon; its constitutional formula will thus be:  $C_{19}H_{25}(OH)_5.O_2.O_3$ . From the acetyl-derivatives saponine can be regenerated.

V. H. V.

**Specific Rotatory Power of Photosantonin Acid.** By R. NASINI (*Gazzetta*, **13**, 375—378).—The only one of the five isomeric acids  $C_{15}H_{20}O_4$  which has not as yet been examined optically is the photosantonin acid produced by the action of sunlight on an alcoholic solution of santonin. A Cornu's apparatus was employed with sodium flame, and a temperature of  $20^\circ$ . The results obtained with chloroform and alcoholic solutions are given in the Tables I and II, where  $c$  is the concentration, that is, the weight of substance dissolved in 100 c.c. of the solvent;  $L = 219.65$  the length of the tube in millimetres;  $\alpha$  the angle of deviation;  $[\alpha]_D$  the specific rotatory power with respect to the line D =  $\frac{\alpha 10^4}{L \cdot c}$ .

TABLE I.

$c$ .	$\alpha$ .	$[\alpha]_D$ .
1.259	-3.30	-119.3
2.057	-5.10	-112.9
5.758	-14.30	-113.1

TABLE II.

$c$ .	$\alpha$ .	$[\alpha]_D$ .
0.536	-1.40	-118.9
0.968	-2.50	-117.6
3.285	-9.05	-125.4
4.774	-13.13	-125.2

The following gives the rotatory power of the five acids:—

Santoninic acid	{	(alcohol, $c = 1$ to $3$ )	....	$[\alpha]_D = -25$
Santonin acid		(chloroform, $c = 4.476$ )	....	„ = -70.31
Parasantonin acid	{	„	$c = 4.470$ )	.... „ = -98.51
Metasantonin acid		„	$c = 4.127$ )	.... „ = -92.8
Photosantonin acid	{	„	$c = 1.259$ to $5.758$ )	„ = -119.3 to 113.1
„		(alcohol, $c = 0.536$ to $4.774$ )	„	= -119 to 125

C. E. G.

**Hydronicotine and Oxytrinicotine.** By A. ÉTARD (*Compt. rend.*, **97**, 1218—1221).—5 grams of nicotine, 5 grams of red phosphorus, and 60 grams of fuming hydriodic acid were heated in sealed tubes at  $260$ — $270^\circ$  for 10 hours. Hydrogen was liberated and the crystalline contents of the tube, consisting probably of a periodide, were treated with potash, and the liberated oily bases fractionated. The products thus obtained are a small quantity of hydrocollidine, boiling at  $205^\circ$ , nicotine boiling at  $244^\circ$ , and hydronicotine,  $C_{10}H_{16}N_2$ , an oily liquid which boils at  $263$ — $264^\circ$ ; sp. gr. at  $17^\circ = 0.993$ . It has a faint odour and dissolves in water, alcohol, and ether in all proportions. Hydronicotine is lævogyrate, its specific rotatory power being  $[\alpha]_D = -15^\circ 40'$ . The specific rotatory power of nicotine in solutions



of the same strength (13·7 per cent.) is  $73^{\circ} 6$ , but diminishes with dilution. Acids dissolve hydronicotine with development of heat, but alkalis precipitate the base from its solutions. Hydronicotine platinochloride,  $C_{10}H_{16}N_2H_2PtCl_6 + H_2O$ , forms pale yellow crystals which separate out even from very dilute solutions, and are thus distinguished from nicotine platinochloride. They lose their water in dry air. Hydronicotine hydrochloride gives no precipitate with gold chloride, and is not acted on by dilute solutions of mercuric chloride, potassium dichromate, or ferrous or ferric salts in the cold.

Hydriodic acid under pressure is the only substance with which the author has been able to obtain hydronicotine.

*Oxytrinicotine*.—Nicotine is heated to  $240^{\circ}$  and mercuric oxide is added in small quantities at a time until the liquid becomes thick and brown. Each addition of the oxide produces an energetic reaction; water is given off and metallic mercury separates out. The product of the reaction is allowed to cool, dissolved in dilute hydrochloric acid, and the solution filtered. The filtrate is treated with hydrogen sulphide, filtered from the mercuric sulphide, and the dark brownish-black filtrate is mixed with an alkali, which produces a flocculent brown precipitate of the composition  $C_{30}H_{27}N_6O_2$  or  $(C_{10}H_9N_2)_3O_2$ , analogous to thiotetrapyridine,  $(C_{10}H_9N_2)_2S$ . This substance may be regarded as formed in a similar manner to thiotetrapyridine, the mercuric oxide giving up its oxygen at  $240^{\circ}$  in presence of the organic compound, and the author proposes to call it oxytrinicotine. Oxytrinicotine hydrochloride does not crystallise, and, like thiotetrapyridine hydrochloride, has an astringent taste. With platinum chloride its solution yields a brownish-yellow precipitate of the composition  $(C_{10}H_9N_2)_3O_2 \cdot 2H_2PtCl_6 + 6H_2O$ . C. H. B.

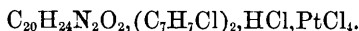
**Mono- and Di-chloracetate of Quinine.** By G. MAZZARA (*Gazzetta*, 13, 525—527).—These salts,  $CH_2Cl \cdot COOH \cdot C_{20}H_{24}N_2O_2 \cdot 2\frac{1}{2}H_2O$  and  $CHCl_2 \cdot COOH \cdot C_{20}H_{24}N_2O_2 \cdot 2H_2O$ , are prepared by adding the requisite quantities of quinine dissolved in alcohol to mono- and dichloracetic acid respectively, and gently heating the mixtures. They crystallise in white silky needles, and dissolve in water; the mono-chloracetate in 62·43 parts at  $20^{\circ} 9$ , the dichloracetate in 41·4 parts at  $22^{\circ}$ . H. W.

**Action of Benzyl Chloride on Quinine.** By G. MAZZARA and G. POSSETTO (*Gazzetta*, 13, 529—532).—When these two bodies are heated together in alcoholic solution, a deep red liquid is formed, leaving on evaporation a residue of similar colour, which dissolves partially in water, leaving a resinous substance. The solution thus obtained is dichroic, yellow by transmitted, red by reflected light, and yields with platinic chloride a precipitate which dissolves in dilute alcohol, and separates therefrom as a micro-crystalline mass, having the composition  $C_{20}H_{24}N_2O_2 \cdot C_7H_7Cl \cdot HCl \cdot PtCl_4 + 2H_2O$ .

The concentrated solution of the compound of benzyl chloride and quinine gives with caustic soda a greenish-yellow precipitate; the dilute solution, a yellow crystalline precipitate of a compound of quinine with benzyl alcohol, which melts and blackens at  $75^{\circ}$ , dissolves

in cold alcohol and ether, and melts to a resin when heated with water or alcohol.

The aqueous solution of the compound of benzyl chloride and quinine leaves on evaporation a yellowish semi-solid residue, and on heating this substance (8 g.) dissolved in alcohol with an equimolecular quantity of benzyl chloride (2.2 g.), and evaporating the alcohol, a deep red viscid residue is left, which dissolves partly in water, forming a solution green by transparent, red by reflected light. This solution, treated with platinic chloride, forms a yellow precipitate soluble in dilute alcohol, from which it is deposited in the form of a light friable powder, having the composition



The solution of the compound of benzyl chloride and quinine, mixed with excess of water and caustic soda, yields a deep yellow precipitate which melts at  $85^\circ$  and decomposes at  $130^\circ$ , with emission of gas-bubbles.

A mixture of benzyl chloride and *benzylquinine hydrate*, in molecular proportion, dissolved in alcohol and treated as above, yielded a product which, when freed from alcohol and treated with water, formed a deep red solution, giving with platinic chloride a brick-red precipitate having the composition  $\text{C}_{20}\text{H}_{24}(\text{C}_7\text{H}_7)\text{N}_2\text{O}_2, \text{C}_7\text{H}_7\text{Cl}, \text{HCl}, \text{PtCl}_4$ .

H. W.

**Action of Aromatic Aldehydes on Quinine.** By G. MAZZARA (*Gazzetta*, **13**, 367—369).—After referring to his former experiments on aldehydic compounds of quinine (this vol., 186), the author states that whilst nitrobenzaldehyde gives comparatively stable compounds with quinine, the results obtained with paraldehyde benzaldehyde and anisaldehyde are unsatisfactory.

When quinine and nitrobenzaldehyde in molecular proportions are boiled together in chloroform solution, and ether is added to the product, a yellow gelatinous precipitate is obtained resembling alumina in appearance. When dried, it is a yellow powder which melts at  $113$ — $118^\circ$ . It has the composition  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2, \text{C}_6\text{H}_4(\text{NO}_2).\text{CHO}$ . It is easily decomposed by acids into a salt of quinine and nitrobenzaldehyde.

If the chloroform solution of quinine and nitrobenzaldehyde is allowed to evaporate spontaneously instead of being precipitated with ether, a yellowish viscid residue is left which turns brown on exposure to the air.

C. E. G.

**Caffeine, Xanthine, and Guanine.** Part II. By E. FISCHER and L. REESE (*Annalen*, **221**, 336—344).—*Chlorocaffeine* is best prepared by passing chlorine gas which has been dried by means of sulphuric acid and phosphoric anhydride, into a boiling solution of caffeine (dried at  $120^\circ$ ) in chloroform. The operation is ended when the evolution of hydrochloric acid ceases. Chlorocaffeine may with great advantage be substituted for bromocaffeine in the preparation of the compounds described in Part I (Abstr., 1883, 354).

*Diethoxyhydroxycaffeine*,  $\text{C}_8\text{H}_9\text{N}_4\text{O}_2(\text{OH})(\text{OEt})_2$ , is decomposed by hydriodic acid, yielding hydroxycaffeine. The reaction takes place

most favourably in a chloroform solution. Diethoxyhydroxycaffeine dissolves in phosphorus oxychloride, forming the compound



This derivative is reconverted by alcohol into diethoxyhydroxycaffeine. It is completely decomposed by water, with the formation of a considerable quantity of dimethylalloxan.

The decomposition of *Amalic acid*,  $\text{C}_{12}\text{H}_{14}\text{N}_4\text{O}_8$ , by heat is very complicated. One of the products of decomposition is *deoxyamalic acid*,  $\text{C}_{12}\text{H}_{14}\text{N}_4\text{O}_6$ . It is a colourless crystalline body, freely soluble in chloroform and strong acetic acid. It melts at  $260^\circ$  and sublimes at the same temperature. At a higher temperature, it distils with partial decomposition. On evaporation with nitric acid, dimethylalloxan is formed. Since prolonged boiling with chromic mixture converts deoxyamalic acid into dimethylparabanic acid, this acid is probably a derivative of malonyldimethylcarbamide.

*Bromoguanine*,  $\text{C}_5\text{H}_4\text{N}_4\text{OBr}$ , obtained by the method adopted for the preparation of bromocaffeine, is a white crystalline powder, almost insoluble in alcohol, ether, and cold water. It unites with acids to form crystalline salts, e.g.,  $\text{C}_5\text{H}_4\text{N}_4\text{O} \cdot \text{Br} \cdot \text{HCl}$ , and also with lead and silver to yield crystalline compounds. A complicated reaction takes place when the silver or lead salt is heated with methyl iodide at  $100^\circ$ . No methyl-derivative is obtained, but a considerable quantity of bromocaffeine is produced. Nitrous acid converts bromoguanine into *bromoxanthine*. This crystalline compound is decomposed by heat without melting. It is soluble in hot water, hot alcohol, and in mineral acids, but it is insoluble in alkalis. W. C. W.

**Piperylhiazine.** By L. KNORR (*Annalen*, **221**, 297—313).—The preparation of *piperylhiazine* by the action of zinc-dust and acetic acid on nitroso-piperidine has been previously described by the author (Abstr., 1882, 1115). It is a colourless refractive oil of ammoniacal odour. It boils at  $146^\circ$ , and has a sp. gr. 0.928 at  $14.6^\circ$  compared with water at the same temperature. Piperylhiazine is very hygroscopic. It is miscible in all proportions with water, alcohol, ether, and benzene, but is sparingly soluble in concentrated solutions of the alkalis. It precipitates metallic oxides from their solutions, and expels ammonia from hot solutions of its salts. With chloroform and potash, it exhibits the isonitrile reaction, and it reduces cold ammoniacal solutions of silver, and also Fehling's solution on warming. Mercuric oxide, potassium permanganate, and bromine-water oxidise piperylhiazine, and convert it into the corresponding tetrazone. *Piperylhiazine hydrochloride*,  $\text{C}_6\text{H}_{10}\text{N} \cdot \text{NH}_2 \cdot \text{HCl}$ , is deposited from alcohol in plates melting at  $162^\circ$ , which are freely soluble in hot water and chloroform. The platinochloride is insoluble in alcohol and ether. The picrate forms golden-yellow needles.

*Monobenzoylpiperylhiazine*,  $\text{C}_6\text{H}_{10}\text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ , is deposited in white scales on mixing together ethereal solutions of benzoic chloride and piperylhiazine. The crystals melt at  $195^\circ$ , and distil at a higher

temperature without decomposition. When benzaldehyde and piperylhydrazine are brought together, *benzylidenepiperylhydrazine*,



melting at  $62^\circ$ , is produced. It is deposited from a hot alcoholic solution in crystalline plates, soluble in alcohol and ether.

*Piperylsemicarbazide*,  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{NH}\cdot\text{CONH}_2$ , prepared by the action of potassium cyanate on piperylhydrazine hydrochloride, forms rhombic crystals melting at  $136^\circ$ , which dissolve freely in alcohol and in hot water.

*Piperylthiosemicarbazide*,  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{NH}\cdot\text{CSNH}_2$ , is prepared from piperylhydrazine hydrochloride and ammonium thiocyanate by Fischer and Besthorn's method (*Annalen*, **212**, 325). It crystallises in prisms melting at  $167^\circ$ , and soluble in alcohol.

Carbon bisulphide acts energetically on piperylhydrazine; in presence of alcohol, *piperylthiocarbazine*,  $\text{CS}(\text{NH}\cdot\text{NC}_5\text{H}_{10})_2$ , is the result of the reaction. This compound crystallises in transparent rhombic plates melting at  $181^\circ$ , which are freely soluble in alcohol and benzene. A *dipiperylthiosemicarbazide*,  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CS}\cdot\text{NH}\cdot\text{NC}_5\text{H}_{10}$ , was also obtained crystallising in the triclinic system. It melts at  $85\cdot5^\circ$ , and decomposes at a higher temperature.

Piperylhydrazine is decomposed by nitrous acid into nitrosopiperidine and nitric oxide. It unites with methyl iodide to form *methylpiperylazonium iodide*,  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{NH}_2\text{MeI}$ , which crystallises in needles, soluble in water, chloroform, and hot alcohol. The compound begins to decompose at  $150^\circ$ . The iodide is converted into *methylpiperylazonium hydroxide* on treatment with silver oxide. This base is decomposed by heat, yielding dimethylpiperylammonium iodide, piperidine, ammonia, and other products.

The preparation of the *tetrazone* has been previously described (*loc. cit.*). Acid solutions of the tetrazone are very unstable; they are decomposed by heat, half the nitrogen is evolved, and piperidine is formed. The *hydrochloride* is obtained as a heavy oil on mixing ethereal solutions of hydrochloric acid and the tetrazone. The *platinochloride*,  $(\text{C}_{10}\text{H}_{20}\text{N}_4)_2\cdot\text{H}_2\text{PtCl}_6$ , is an amorphous powder, decomposing with detonation at  $70^\circ$ .  
W. C. W.

**Action of Bromine on Pilocarpine.** By CHASTAING (*Compt. rend.*, **97**, 1435—1437).—When bromine is added to a solution of pilocarpine in chloroform, there is development of heat, the mixture becomes acid, and a heavy oily liquid separates. The supernatant chloroform retains the excess of bromine together with a small quantity of the bromo-derivative, which gradually crystallises out. The oily liquid is rapidly evaporated, and forms a deep golden-yellow resinous mass, which is then dissolved in chloroform, from which it separates in a mass of minute prismatic crystals. These crystals have the composition  $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}_2\text{Br}_5$ , and consist of a *dibromide of dibromopilocarpine hydrobromide*,  $\text{C}_{11}\text{H}_{14}\text{Br}_2\text{N}_2\text{O}_2\cdot\text{HBr}\cdot\text{Br}_2$ . This substance is inodorous, but when exposed to air it absorbs moisture and gives off ethyl bromide, undergoing some alteration which results in the formation of a compound containing less carbon than the original

substance. In contact with copper, dibromide of dibromopilocarpine hydrobromide gives up part of its bromine, and when treated with silver oxide in presence of water and chloroform, it loses  $\text{Br}_3$  and yields dibromopilocarpine,  $\text{C}_{11}\text{H}_{14}\text{Br}_2\text{N}_2\text{O}_2$ , which resembles pilocarpine in appearance, but is less mobile and less strongly alkaline; it is precipitated by platinum chloride.

The action of bromine on pilocarpine in presence of a small quantity of water does not yield dibromide of dibromopilocarpine hydrobromide, but the corresponding derivative of a feebler base which contains an atom of carbon less than pilocarpine. This carbon is given off as carbonic anhydride, and the compound formed should be represented by the formula  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2, \text{HBr}, \text{Br}_2$ . C. H. B.

**Ptomaines and their Significance in Toxicology.** By T. HUSEMANN (*Arch. Pharm.* [3], 21, 401—417).—The commencement of a history of the ptomaines, and the methods of detecting them and distinguishing them from vegetable alkaloïds, compiled from the papers of recent investigators. W. R. D.

**Ptomaines and Similar Bodies.** By C. ARNOLD (*Arch. Pharm.* [3], 21, 435—437).—In the course of a toxicological examination of the stomach and intestines of five dogs and two horses by the Stas-Otto method, the author isolated a brown viscous liquid having a strongly alkaline reaction, an aromatic smell, and a bitter taste. When neutralised with hydrochloric acid, it yielded a distinctly crystalline salt. The contents of the stomachs of seven dogs recently killed with hydrocyanic acid were examined for the same substance, and in four instances it was obtained. The weight of the product was two or three centigrams. It yielded precipitates with all the usual alkaloïd reagents, and when neutralised with hydrochloric acid and subcutaneously injected in frogs, it caused temporary paralysis. Rabbits were not affected when similarly treated. The alkaloïd could not be extracted from the brains, spleen, liver, or other organs of the animals; but in two cases when the fresh urine was treated by the Stas-Otto process, a residue which gave the general reactions for alkaloïds was isolated. An attempt was now made to produce the same alkaloïdal substance by a process of artificial digestion. 5 grams of pepsin and 100 grams of freshly prepared fibrin were mixed with 2.5 litres of water, to which had been added 25 grams of hydrochloric acid (sp. gr. 1.125). The mixture was allowed to stand for 30 hours at  $37\text{--}38^\circ$ , after which it was treated by the Stas-Otto method, and 0.4 gram of a body was obtained which had the same chemical, physical, and physiological properties as that which had been extracted from the actual contents of the stomach. The author has been easily able to isolate ptomaines from putrefying animal corpses. From 500 grams of the muscular tissue of a dog, in a high state of decomposition, 1.6 grams of a volatile alkaloïd was obtained by the Stas-Otto method; when it was subcutaneously injected in a rabbit, tetanus and death ensued. From 500 grams of putrefying horse-flesh 0.5 gram of the same substance was obtained. W. R. D.

## Physiological Chemistry.

**Effects of Rarefied Air on the Animal Organism.** By A. FRANKEL and J. GEPPERT (*Bied. Centr.*, 1883, 599—601).—Dogs were the animals experimented on; the general appearance of respiration under continuously reduced pressure coincides with the observations of Bert and with the experience of aëronauts at high elevations. It is remarked that the organs of the animals which were usually experimented on showed symptoms of gradually adapting themselves to their conditions, so that to obtain trustworthy results they should be allowed intervals of days, and even a week, and that those animals would bear with impunity increase and diminution of atmospheric pressure which a newly employed animal would not. A rarefaction equal to an elevation of 3800—4900 meters showed no perceptible diminution in the oxygen contained in the blood of three dogs, and with five others the loss was very small. At a pressure diminished to half an atmosphere the oxygen began to vary, but still very nearly within normal limits, so that probably the diminution of oxygen in the rarefied air was compensated by the rapidity of respiration. A reduction of pressure to one-third of an atmosphere impoverished the blood rapidly, and at one-fourth of an atmosphere death followed; at one-third, arterial blood contains only one-half its normal proportion of oxygen. The authors' experience confirms Bert's opinion that the effect of diminished barometrical pressure on the animal economy is within certain limits of a chemical rather than mechanical nature, and that even the bleeding which takes place from thin membranes is due to their having been weakened by abstraction of oxygen. A considerable increase in the nitrogen voided by the animals in their urine under diminished pressure was also noted.

J. F.

**Experiments on the Time Required for Digestion of Meat and Milk.** By E. JESSEN (*Bied. Centr.*, 1883, 602—604).—These experiments were of three classes; with an artificial digestive solution the substances introduced into the stomach of a dog and of a man.

The meat employed was separated from sinews and chopped small; it was used raw, half boiled, and well boiled, half and well roasted, the latter with 5 grams of butter to 100 grams of meat. Two strengths of pepsin solution were used, one containing 0.1 per cent. pepsin and  $2\frac{1}{2}$  per cent. hydrochloric acid, the other double the strength, both appeared to have the same amount of digestive power; the solutions were left in contact with the meat for 24 hours at a temperature of 35—40°. The undigested portion of the meat was then separated by filtration, dried at 110°, and weighed; the residues from 25 grams were—

Raw flesh .....	5.67
Half boiled.....	9.49
Well boiled .....	17.95
Half roasted .....	9.76
Well roasted .....	17.07

The experiment on the dog was made by introducing the meat sewn in a netting bag through a fistula into the stomach; 2 grams were used, the digestive power being previously excited by a ration of bread and milk. Owing to the meat not being freely accessible, the time of digestion was long, but conditions being the same, the results are useful for comparison. The time occupied in digestion of 2 grams—

	Hours.
Raw beef .....	5.58
Half boiled .....	6.83
Well boiled .....	5.79
Half roasted.....	7.42
Well roasted.....	7.54
Frog's flesh .....	4.46
Veal .....	6.63
Pork .....	6.25

A man, 30 years old, in normal health, was the subject of the next experiment. When his stomach was pumped empty he was fed with 100 grams meat and 300 c.c. water. The experiment was considered at an end when the stomach-pump brought up no particles of fibrine. The time required for digestion of the different substances:—

	Hours.
Raw beef .....	2
Half boiled .....	2½
Well boiled .....	3
Half roasted.....	3
Well roasted.....	4
Raw mutton .....	2
Raw veal .....	2½
Raw pork .....	3

The same person was fed with milk, the nitrogenous contents of which equalled those of 100 grams beef—

	Hours.
602 c.c. raw cows' milk.....	3½
602 „ boiled „ .....	4
602 „ sour „ .....	3
675 „ skimmed „ .....	3½
656 „ raw goat's milk .....	3½

J. F.

**Digestive Power of Commercial Pepsin.** By C. M. DANA (*Bied. Centr.*, 1883, 644).—A number of samples of American and German preparations of pepsin dissolved on an average 10—12 times their weight of coagulated albumin, but were almost without result on larger pieces. To prove that this does not resemble the natural action of the stomach, the author experimented on dogs. The animals were fed with hard boiled eggs and meat, with and without pepsin; in the latter case (15 dogs) but one-third of the albumin dissolved; whilst with 21 dogs which had received pepsin, but one-fifth remained undissolved, and some which had got a better pepsin, only one-eighth

remained undissolved. The duration of digestion was  $1\frac{3}{4}$  to  $3\frac{1}{2}$  hours: the operations in the stomach were therefore better than outside.

J. F.

**Behaviour of Amides in Animal Nutrition.** By N. ZUNTZ (*Bied. Centr.*, 1883, 602) —The experiments undertaken to verify those of Weiske (*Abstr.*, 1882, 986) were performed on rabbits, which received as food 13 grams rice-starch freed from albumin by pepsin and hydrochloric acid, 2 grams sugar-candy, 2 grams olive oil, and 0.33 gram of the neutral ash of hay and wheat with 0.09 of common salt. When to this food, free from nitrogen, was added 1.5 gram of asparagine, there was an immediate reduction of the loss of nitrogen from the body amounting to from 71 to 72 per cent.; when in addition 0.1 gram tyrosine, 0.05 gram taurine, and 0.05 gram of guanidine thiocyanate were given, the waste of albumin *increased* by 156 per cent. above that of non-nitrogenous food. If a part of the asparagine is replaced by a strong ammonium body, produced by the action of pancreatic fluid on meat, the waste of nitrogen became 1.7 per cent. higher than when non-nitrogenous food was given.

J. F.

**Experiments with Stall-fed Cattle.** By VOSSLER (*Bied. Centr.*, 1883, 512—614).—The experiments were made to ascertain if well fattened cattle could be maintained in that state for a lengthened period on moderate rations, if kept in a state of rest as nearly perfect as possible. Ewes and oxen were so treated, and with success; although the fattening was finished previous to the experiment, they did not lose but in some cases gained weight.

J. F.

**Further Experiments on the Digestive Powers of the Horse.** By v. ELLENBERGER and V. HOFMEISTER (*Bied. Centr.*, 1883, 604—606).—In continuation of his researches (*Abstr.*, 1883, 487, and this vol. 92), the authors submitted the mucous membrane of the horse's stomach to a complete histological examination. The gullet end of the stomach forms a receptacle in which the saliva has time to act on the large quantities of starchy matter which constitute the food of the horse, not being furnished with the glands which secrete the acid gastric juice; the posterior portion being furnished with those glands; the stomach is comparatively small but very elastic, and surrounded by strong and elastic integuments, its walls contain intercellular and intermuscular ganglia, and at least three kinds of cells, the peculiarities of which have not been fully examined. The cells of the pylorus glands, too, differ from those of the intestine.

The pepsin present in the mucous membrane of the stomach is partly extracted by glycerol and partly by treatment with hydrochloric acid. That part of the stomach which produces pepsin is small in extent, but very thick and has long capillaries. The surface of the pylorus contains very little trace of pepsin in the first hours of digestion, and not much at any period, but it is very abundantly produced in the proper part of the stomach, and possesses stronger fermentative qualities in those glands which lie deepest beneath the surface, and its greatest strength is about the end of the digestive process.

J. F.



**Feeding Experiments on Pigeons.** By ASSMUS (*Bied. Centr.*, 1883, 857).—A cock and a hen pigeon which originally weighed 200 and 250 grams respectively, after eating 75 grams daily of a mixture of 1 flesh meal and 10 potatoes for 20 days, were found to have increased in weight by 80 and 70 grams. E. W. P.

**"Champion Spice."** By C. LEHMANN and others (*Bied. Centr.*, 1883, 826).—A spice is much sold which is supposed greatly to increase the flow of milk when added to ordinary food. The authors state that such is not the case, but rather that the yield is reduced; they state that this spice consists of the waste from the grinding of *Fœnum græcum*, coriander, cumin, and aniseed, which is mixed with a little palm-nut cake.

The following figures show the difference between the guaranteed analysis and that made by one of the authors:—

	Guaranteed.	Siewert.
Fat .....	3·64	2·54
Albumin .....	10·76	4·55
Fibre and carbohydrates ..	70·24	60·61
Water .....	10·25	9·74
Sand and ash .....	5·11	9·16

E. W. P.

**Cattle Plague and Pasteur's Protective Inoculation.** By MÜLLER and others (*Bied. Centr.*, 1883, 614—618).—The first part of this paper is a report on certain herds of oxen and sheep which had been inoculated with Pasteur's so-called vaccine; it shows that the loss by death from the disease was very much less than amongst unprotected animals.

Archangelske describes his researches on the development of the bacteria of splenic fever. From the moment of the infection, the blood of the animal (using every possible caution in the examination) contained small round shining spherical organisms, about the size of ordinary micrococci; a little of this blood added to chicken broth caused cloudiness next day from presence of the bacteria. In the second stage of culture, bacteria and thread-like bodies were present, the latter developed themselves on potatoes, and mice died when they were introduced into their system; all the animals from which the blood was drawn died of splenic fever, with bacteria in the blood, spleen, and other organs. The author thinks these globular bodies are the spores of the bacteria, which multiply in the earlier stages and develop bacteria at the end of the sickness; the development in the earlier stages can be ascribed only to a splitting up similar to that of micrococci. As death sometimes occurs previous to the development of the spores, it accounts for some observers not having found bacteria after death; the author mentions a theory of Lemmers that the two forms are those of two different organisms, one of which being numerous while the other is few, and the reverse.

Feltz has investigated the part which earthworms are said to play in the spread of the disease; infected blood from artificial culture, and from guinea-pigs which died of the disease, was mixed with

earth and placed in a flower-pot, in which were also placed worms; at intervals during 22—52 days worms were withdrawn and washed repeatedly in distilled water. Guinea-pigs were then inoculated with matter from the cut-up worms, and also the water in which they had been washed; the contents of the worms and the first washings produced the disease, but the last wash-water did not. Feltz also made experiments on rabbits in order to weaken the infection, but the results were unsatisfactory. He says that a long contact with the soil weakens the germs, and that a milder form of fever follows when derived from such a source. J. F.

**Effects of Copper on the Organism of Ruminants.** By v. ELLENBERGER and V. HOFMEISTER (*Bied. Centr.*, 1883, 606—609).—The action of solutions of salts of copper on animal membranes has long been known and investigated, but much remains to be learned, especially about chronic copper poisoning. The authors limit their work to a record of observations on the effects of small doses of the salts regularly administered. The subjects of the experiment were sheep, and the dose of from half a gram to 3 grams. Amongst the negative results were no alteration of muscular structure, no acceleration of the motion of the heart, no uniform alteration in the microscopic appearance of the blood corpuscles, no alteration of the respiration nor of the secretion of urine. Amongst the positive results, the presence of albumin, bile, and blood in the urine, flaccidity of muscles, weakness, and loss of appetite. The excretion of copper from the system is chiefly by means of the bile, partly by the urine, but in lesser degree.

The principal part of the body which retains copper is the liver, which holds it with very great tenacity, having been found 41 days after a dose had been given; the pancreatic glands retain it with almost equal strength; the kidneys do not contain so much as the other two organs. The deposit of copper is proportionally much greater if it has been administered in numerous small doses, the cells having time to absorb it, which is not the case with large doses, owing to their rapid action. The deposits in the nervous system are small, and still smaller in the muscular, not enough to interfere with their action, but sufficient to be found in the flesh after administration of medicines containing copper. J. F.

**Kairine and Kairoline—Hydroxyquinolinemethyl Hydride and Quinolinemethyl Hydride.** By FILEHNE (*Pharm. J. Trans.* [3], 14, 383—384).—The present paper treats of the physiological properties of these bodies. They are both, as well as some other compounds of the quinoline series, very powerful anti-pyretics, but have no local action, and are, therefore, valuable medicines in cases of fever. They are quite similar in action; kairoline is, however, less energetic and slower in action than kairine. Kairine has been tried in a series of acute and chronic febrile diseases, and in all, its antithermic action was found to be constant.

The hydrochloride is the salt employed; it is a clear crystalline greyish-yellow powder, very soluble in water, and has a bitter some-

what aromatic taste. After administering the powder, water should be drunk freely. Its use is not accompanied by any unpleasant effects, such as headache, ringing in the ears, sickness, &c. With regard to its antithermic properties, doses of 1 to 1.5 gram in healthy adults have no physiological action and no effect on the temperature; whilst in cases of adult patients or debilitated subjects, a dose of 1 gram every two hours must not be exceeded, otherwise cyanosis is apt to ensue. The most suitable dose in adult fever cases is 0.3 to 0.5 gram every hour or  $1\frac{1}{2}$  hour. The interval between 1 gram doses should not exceed  $2\frac{1}{2}$  hours, and that between 0.5 gram doses not more than  $1\frac{1}{2}$  to 2 hours, for the effect of 1 gram only last three hours, whilst that of 0.5 gram is of  $2\frac{1}{4}$  hours' duration; to produce a less pronounced effect reduce the doses, but do not increase the interval. When the influence of the drug ceases, the temperature rises again with a feeling of chilliness amounting sometimes to actual rigor. Less than 0.3 gram given at once has no practical effect on the temperature, a dose of 0.3 to 1 gram lowers the temperature by  $\frac{1}{2}$  to  $2^{\circ}$ , another dose given before the effect of the former one passes away, causes a further reduction, and if 0.5 gram be given hourly, it invariably follows that, without any injurious effect, the temperature falls to the normal point or below it after the fourth (sometimes after the third, or even the second) dose. The temperature cannot be brought below  $37-36.5^{\circ}$ , and the low temperature is maintained only as long as the administration of the drug is continued every  $2\frac{1}{2}$  hours at least, otherwise shivering occurs, and the temperature rises to the point corresponding to the acuteness of the disease; this drawback is overcome, so as not to disturb the night's rest, by judicious dosing during the day, and by giving a full dose of 2 grams of *kairoline* the last thing at night. The action of kairine begins 25 minutes after the dose of 0.5 to 1 gram is taken by the mouth; the fall in temperature is more rapid the larger the dose, and is always accompanied by profuse sweating, which lasts only as long as the temperature continues to fall. During the use of these drugs, the urine becomes green, but contains no sugar or albumin. Pneumonia patients especially have enjoyed great comfort from the use of this drug; in fact, such cases can be kept quite free of fever. It is suggested to use kairine as a remedy in malarial affections, by giving 1 gram hourly, three hours before the expected attacks.

D. A. L.

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### Chemistry of Vegetable Physiology and Agriculture.

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**Influence of Light on the Development of Bacteria.** By J. JAMIESON (*Bied. Centr.*, 1883, 857).—Bacteria were destroyed by direct sunlight, but not by diffused light. The experiments showed that at a moderate or low temperature the direct sunlight had no destructive action. Dry bacteria were killed in three or four days

when exposed to sunlight and air. From this it is evident that the action of light on bacteria is not yet accurately ascertained.

E. W. P.

**Occurrence of the Butyric Ferment.** By W. ZOPF (*Bied. Centr.*, 1883, 858).—The saccharine matter of plants, cucumbers, cabbages, &c., is first converted by the lactic ferment, which is probably only a variety of *Clostridium butyricum*, into lactic acid, then the true butyric ferment begins its work. Upon this process depends the ripening of cheese and formation of sauer kraut.

E. W. P.

**Yeast.** (*Dingl. polyt. J.*, 249, 227, 231).—According to Delbrück alcohol and sulphuric acid have peculiar influence on both yeast and bacteria. They are both poisonous for bacteria, and both prevent the growth of yeast without however destroying its fermentative power. A very large amount of sulphuric acid may be present, for an hour at least, without destroying this power, but no increase of the cells takes place. Similarly in the mash, the presence of 5 to 7 per cent. of alcohol prevents growth in the yeast, but the fermentative power remains. Heinzelmann has found that 0.1 gram of salicylic acid to the litre of yeast increases its fermentative power, 0.12 gram begins to diminish this power, and with 0.375 gram the yeast is killed. 200 grams malt mashed to 1 litre, and treated with 0.1 gram salicylic acid, gave a better sugaring and stronger fermentation than without the acid, so that it appears advisable to add the acid to the yeast preparation, and then to prepare the mash in the usual manner.

Lintner, investigating the formation of diastase under various conditions, could only obtain accordant results with the same barley after careful drying at 50°. Moist and bad barley so treated give very uniform results.

J. T.

**Formation and Accumulation of Saccharose in the Beet.** By A. GIRARD (*Compt. rend.*, 97, 1305—1308).—The author confirms Peligot's statement that the root never contains any sugar but saccharose, and finds that saccharose exists together with glucose not only in the petioles and ribs, but also in the blade of the leaves. The root and its beard, and the petioles, have the same composition in the night as in the day, but the proportion of saccharose in the blades varies, and is frequently twice as great in the evening as it is the next morning. The quantity of glucose in the blades is sensibly the same at night as in the morning, and increases only with the development of the plant. The proportion of saccharose, however, depends on the amount of light that the plant has recently received, and at the close of a bright day may approach 1 per cent., but at the close of a dull day it is considerably less. In all cases, however, about half and sometimes even a higher proportion of the saccharose formed during the day disappears from the blades during the night. The composition of the petioles connected with the midribs undergoes no sensible diurnal variation. It would seem, therefore, that the saccharose is first formed directly in the blades under the influence of light, and is afterwards transported through the petioles to the roots, where it is gradually stored up. Since the leaves increase in bulk,

but retain the same percentage of inorganic matter, it seems probable that a double osmotic movement takes place in the plant by which the inorganic substances absorbed from the soil are transported to the leaves, whilst the saccharose formed in the leaves is transported to the root.

C. H. B.

**Ratio of Flesh to Stone in Stone Fruit.** By G. WILHELM (*Bied. Centr.*, 1883, 851).—

	Reine Claude. Per cent.	Damask plum. Per cent.
Flesh .....	96·00	96·05
Stone { shell .....	3·17	2·81
{ kernel.....	0·83	0·91
Stem .....	—	0·23
	<hr/> 100·00	<hr/> 100·00

E. W. P.

**Chemical Changes in Decayed Wood.** By A. WAGNER (*Dingl. polyt. J.*, 249, 342—346).—Timbers undergoing three different kinds of decay were examined:—(a) red rot; (b) white rot; and (c) that produced by *Merulius destruens*. The composition of the rotten timbers in all three cases did not deviate much from that of sound timber, although the physical change was so great.

	a.	b.	c.
Water .....	9·9	11·71	17·12
Ash .....	3·35	1·77	2·41

Dried at 100° they gave respectively—

C .....	50·04	50·89	51·16
H .....	6·48	6·37	4·70
O and N .....	39·77	40·74	41·24
Ash .....	3·71	2·00	2·90
SO <sub>3</sub> in ash .....	6·41	3·35	1·54

The high sulphuric anhydride in *a* is ascribed to the material with which the timber was in contact.

Boiling water extracts only small quantities from *a* and *b*, producing light yellow solutions, whilst from *c* considerable quantities of organic matter are taken up producing a strong brownish-red solution. Boiling potash-solution is still more striking in its action; *c* is almost completely dissolved with a dark brown colour, whilst *a*, and particularly *b*, are only slightly attacked, with much lighter and more reddish colour.

J. T.

**Elementary Composition of Certain Kinds of Wood, with a Calorimetric Investigation into their Combustibility.** By E. GOTTLIEB (*J. pr. Chem.* [2], 28, 385—421).—The results of the author's analysis of woods from various Danish trees agree on the whole with those of Chevandier and Brix. The following are the

average results obtained from samples taken both from near the roots and near the tops of the trees, and dried at 115°:—

Wood.	Carbon.	Hydrogen.	Oxygen and nitrogen.	Ash.
Oak .....	50·16	6·02	43·45	0·37
Ash .....	49·18	6·27	43·98	0·57
Hornbeam .....	48·99	6·20	44·31	0·50
Beech .....	49·06	6·11	{ 44·17 0·09 }	0·57
Birch .....	48·88	6·06	{ 44·67 0·10 }	0·29
Fir .....	50·36	5·92	{ 43·39 0·05 }	0·28
Pine .....	50·31	6·20	{ 43·08 0·04 }	0·37

The quantity of carbon and hydrogen, however, was found to vary slightly according as the sample was taken near the root or the top in the cases of oak, ash, and hornbeam, but not in the case of beech. A specimen from a beech tree grown on a chalky soil contained less carbon. These results show the quantity of carbon in all the dried samples to be greater than that in cellulose. The small quantities of tannin, resin, fatty or nitrogenous bodies cannot account for this, nor can the author throw any light on the quantity of the substances which raises the total quantity of carbon in wood above that contained in pure cellulose and similar substances. The quantity of nitrogen was never above 0·1 per cent., which is not in accordance with the results (over or about 1 per cent.) of Chevandier. The author describes minutely the form of calorimeter which he constructed and used for obtaining the following results; 1 gram of the substance (dried at 115°) being used:—

	Heat-units.
Oak (180 years old) .....	4620
Hornbeam .....	4728
Beech (60 years old) .....	4766
„ (100 years old) .....	4770
„ (130 years old) .....	4785
Fir (40 years old) .....	5035
Ash .....	4711
Birch .....	4771
Pine .....	5085

According to Dulong, the heat of combustion of a substance may be calculated by adding that of the single parts, abstracting however that of as much hydrogen as is capable of forming water with the oxygen contained in the substance. J. Thomsen, moreover, has shown (*Pogg. Ann.*, 148, 392, and this Journal, 1873, 126) that on burning the hydrocarbons, ethylene and acetylene, the estimated heats of combustion are near the calculated quantities. Calculating, however, by Dulong's formula, the heat of combustion of beech wood and pine

wood respectively, the numbers 4139 and 4240 are obtained, whilst experiment gave 4785 and 5085. Calculating, on the other hand, that the carbon combines completely with the oxygen of the wood to form carbonic acid, and the hydrogen with the oxygen supplied, the numbers 4663 and 4778 are obtained. From this, the author considers that in no case can the heat of combustion be calculated from the results of elementary analysis, the quantity found being always greater. He finds the heat of combustion of pure cellulose (purified and dried cotton-wool) to be 4155, whilst Berthelot found 4142, and v. Rechenberg 4452, and that of charcoal, prepared from pure cotton-wool (containing 96·7 to 96·9 per cent. C, and 1·3 to 1·5 per cent. H), 8033, whilst Favre and Silberman found 8088. A. B.

**Note on Paraguay Tea.** By T. PECKOLT (*Pharm. J. Trans.* [3], 14, 121—124).—This tea is made from *Ilex paraguayensis*, indigenous in the South American region which lies between 18° and 30° S. latitude; it has been planted, and seems to succeed well, in the Cape of Good Hope, Spain, and Portugal. It is stated on experimental evidence, that six different species of the *Ilex* are used in the preparation of this tea. The plant *I. paraguayensis* in the wild state grows to the size of an apple tree, but when cultivated it remains a mere bush. The trees are cultivated from seed, and used when four years old. It is calculated that 1600 trees can be grown on 220 square meters, yielding an average of 35 kilos. per tree. The leaves are collected at different times in different localities, and have most aroma when the fruit is nearly ripe. In some cases the leaves are dried in ovens, in others they are roasted. In the Spanish Republic three different sorts of maté are sold. 1. Caá-cuy or Caá-ciup, the new leaves and scarcely developed shoots, is of a delicate texture and yellow colour, and has an agreeable and pleasant flavour. 2. Caá-mirim, the leaves separated from the twigs and stalks, the mid-rib is also removed from the leaves. 3. Caá-guacu, or Caá-unu, or Jerva de Palos, large old leaves with twigs and fragments of wood, has a strong bitter taste. In Rio Janeiro two sorts are known in commerce—maté leaf and maté powder. Maté has been frequently analysed, and the results have been published from time to time. The author has analysed the fresh leaves, &c., of the *Ilex paraguayensis* from the Orgu Mountains in Neufreieburg, with the following results:—

In the air-dried leaves.	Per 1000
Stearoptene .....	0·021
Volatile oil, extracted by ether.....	0·099
Fat and wax.....	19·800
Green colouring matter .....	10·900
Chlorophyll and soft resin .....	20·966
Brown acid resin.....	48·500
Caffeine.....	6·398
Bitter extractive matter .....	2·033
Sugar .....	39·266
Extractive matter and organic acids.....	8·815
Maté-tannic acid, pure.....	27·472
	2 k 2



In the air-dried leaves.	Per 1000.
Maté-iridic, crystallised.....	0·024
Albumin, organised, inorganic salts, dextrin, &c.....	47·660
Moisture .....	166·660
Cellulose .....	601·356

He has also analysed leaves and maté from Parana, and the quantities of the several constituents in 1000 parts are given in the subjoined table.

	In air-dried leaves, from which maté is prepared.	In commercial maté.
Volatile oil, extracted by ether ..	0·179	0·026
Caffeine.....	16·750	5·550
Chlorophyll and soft resin .....	51·200	16·755
Brown acid resin .....	84·500	25·500
Matétannic acid, pure .....	44·975	16·755
Matéiridic acid, crystalline ....	0·025	0·024
Extractive matter.....	65·130	16·610
Albumin, salts, dextrin, &c. ....	36·102	18·159
Cellular matter and moisture ....	6·643	908·379

Various authors have identified the individual constituents of this substance thus : Trommsdorff found tannin ; Stenhouse, caffeine ; Rochleder recognised the identity of matétannic acid, and caffetannic acid, Hoffmann showed that it was also identical with tannin from tea. Arata distinguishes between the maté- and caffe-tannic acids in this way ; the former requires 73·66 vols. of alcohol for solution, and by dry distillation yields *catechol* and *resorcinol*, whilst the latter requires 52·84 vols. of alcohol, and gives *catechol only* by dry distillation. Soubeiran and Delondre state that maté contains the same essential constituents as coffee-leaf and in greater amount than coffee beans ; the author confirms this statement by numerous experiments. The aromatic principle has not been isolated, but by dry distillation a volatile oil is obtained of phenolic character and soluble in alcohol.

D. A. L.

**Constituents of *Lactarius piperatus* and *Elaphomyces granulatus*.** By T. BISSINGER (*Arch. Pharm.* [3], 21, 321—345).—The author has examined the chief constituents of these fungi. The fat extracted from *Lactarius piperatus* by ether yielded (1) a non-volatile acid melting at 69—70°, having the formula  $C_{15}H_{30}O_2$ . This acid had previously been isolated from the fat of another fungus, *Agaricus integer*, by Thörner (*Abstr.*, 1880, 44) ; (2) a volatile acid, which was proved to be butyric acid ; (3) glycerol ; (4) a substance crystallising from alcohol in rhombic tables melting at 36—37°, which is probably an alcohol of the formula  $C_{14}H_{30}O$ . The non-volatile acid appears to exist in the fat in the free state ; the butyric acid is combined as a glyceride. An analysis of the ash of *Lactarius piperatus* gave the following results expressed as percentage numbers :—

KCl.....	2·41	Fe <sub>2</sub> O <sub>3</sub> .....	3·55
K <sub>2</sub> SO <sub>4</sub> .....	10·40	Mn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .....	0·38
K <sub>2</sub> CO <sub>3</sub> .....	44·76	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .....	0·47
Na <sub>3</sub> PO <sub>4</sub> .....	12·03	CaCO <sub>3</sub> .....	0·62
K <sub>3</sub> PO <sub>4</sub> .....	18·37	MgCO <sub>3</sub> .....	2·66
Fe <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> .....	1·57	SiO <sub>2</sub> .....	3·68

Mannitol was obtained from *Elaphomyces granulatus*; it has previously been found in *Agaricus integer* by Thörner (Abstr., 1880, 44).

W. R. D.

**Vine Diseases and their Remedies.** By H. MÜLLER and others (*Bied. Centr.*, 1883, 630—637).—In the autumn of 1882, the vines of the Rhine provinces of Prussia were attacked by *Peronospora viticola*, and the disease spread rapidly into Hesse, Baden, and Alsace, it was thought, from the course so taken that Gernany proper would not suffer as much as southern lands. An idea prevails that because the disease appears on the leaves only, it is not injurious to the grapes; but the author combats this idea, as the office of the leaves is to form sugar indispensable to the existence of the plant. The organism lives in the interior of the vine-leaf and the buds; on the underside of the leaf it sends out its reproductive organs, delicate filaments with spores at the end of each; one of these if placed on a healthy vine leaf and moistened with a drop of rain or dew suffices to infect it, and it is quickly covered with the white spots denoting the disease; moist weather is therefore most favourable to its propagation. The spores carried to earth by the falling leaves survive in sufficient numbers to propagate the species next season. The author recommends all the leaves to be burned outside the vineyard after the vintage, and the vines washed with a solution of 1 part sulphate of iron in 2 parts water.

Goethe states that during a journey in France he noticed, on the same vines, *Peronospora* and *Torula dissiliens*, causing spots running from light brown to black, and causing the immediate fall of the leaf. Millordet and others describe several other vine diseases, American mildew grape-rust, which he ascribes to the *Phoma uvicola*, which does not itself kill the grapes, but attaches itself to those previously killed by the peronospora.

Amongst the various remedies, besides that before named, is a solution of sodium bicarbonate. F. v. Tchümen describes a fungus which attacks the roots of the vine, *Roesleria hypogæa*, completely destroying the whole stock. This disease has committed great ravages in the department Haute Marne. Moisture is a most favourable condition for the spread of this organism; the only remedy proposed is to pull up the vines by the roots, burn them, and cultivate other crops until the *Roesleria* disappears.

Another disease, *folletage de la vigne*, is distinguished by sudden falling off of leaves and buds, but the vines themselves do not always die.

J. F.

**Phylloxera and Insecticide.** By GIRARDIN and others (*Bied. Centr.*, 1883, 624—625).—Amongst the many remedies proposed for

the extirpation of these ruinous insects, Gerandin says the best results have followed the use of carbon bisulphide and the planting and grafting of American vine stocks. Martin says the stocks should be young and strong. Schule, on the other hand, has not found the planting of American vines to withstand the disease. The use of naphthalene as an insecticide is recommended by Fischer; the trials made with this substance have been numerous, but, apart from its suitability, its comparatively high price is an objection to its use.

J. F.

### **Continuous Cultivation of Wheat and Barley at Woburn.**

By A. VOELCKER (*Bied. Centr.*, 1883, 595—597).—This is a review of the operations at Woburn for the year 1882, as published in the *Journal of the Royal Agricultural Society*. The seed was of the same class as that of the preceding year, Browick wheat. The yield of grain was decidedly smaller than in 1881, but the straw was more abundant, owing to the damp weather. Sodium nitrate, both alone and in combination with other mineral salts, has operated less favourably than in the past year, due probably to the damp also. Mineral manures used alone have produced but a small increase, confirming the results of previous years. Two plots manured the year before with sodium nitrate showed that there was no effective ammonia left in the soil, as they did not this year produce more than others which were unmanured for six years. Yearly applications of mineral manures alone on two other plots failed to give any increased production, whereas on the addition of ammonium sulphate or sodium nitrate the crop was at once trebled. Certain plots strongly manured last year with stable manure prove that there was very little nutritive matter left after the crop had been taken off, and that the ammonia was exhausted in the one season as in the case of the sodium nitrate.

J. F.

**Culture of Cereals.** By MÄRCKER and others (*Bied. Centr.*, 1883, 620—624).—Märcker contributes some notes on the culture of barley. He finds that hoeing more than pays for the additional labour, that a highly nitrogenous manure requires a thinner sowing, and that the distance between the drills largely influences the result. When the field is heavily manured, it is better to have them far apart, but when lightly manured it is better they should be closer together. The experiments are incomplete.

The remainder of the paper contains details of various culture experiments, but they are only of local interest.

J. F.

**Digestibility of Certain Leguminose Straws.** By WEISKE and others (*Bied. Centr.*, 1883, 824—826).—The digestive coefficients of horse-, garden-, and Soja-bean straws as obtained from experiments with sheep, are as follows:—

	Dry matter.	Organic matter.	Albu- min.	Fat.	Fibre.	Extrac- tive.	Ash.
Horse-bean ..	51·77	52·17	47·21	57·21	41·20	64·38	46·49
Garden-bean..	60·83	61·74	53·58	52·58	50·81	72·27	49·30
Soja-bean ....	49·63	52·11	39·41	58·65	42·30	62·80	24·97

E. W. P.

**Sunflower-seed Cake as Fodder for Milch Cows.** By M. SCHRODT and v. PETER (*Bied. Centr.*, 1883, 609—612).—The use of this cake has been strongly recommended and highly praised by observers in Sweden and Denmark as a cheap and valuable fodder. The authors' experiments, however, lead them to different conclusions; the sunflower-seed as compared with palm-nut cake is more costly and produces less milk. The cattle, however, like it and eat it greedily.

J. F.

**Cultivation and Yield of Potatoes.** By O. CIMBAL and others (*Bied. Centr.*, 1883, 828—839).—Cimbal, out of 38 sorts of potatoes, finds Aurora to produce the heaviest yield of starch per acre, and Snowflake the lowest. Nitykowski, near Bremen, finds Imperator the best and Snowflake the worst out of 37 varieties. Sattig considers Gleason's Seed to be the heaviest cropper on heavy land and also on light land, whilst Dabersche is most liable to disease. Yellow Rose, according to Keneman, is the best. J. Timm finds Chicago Early to do best on sandy loam, and Late Rose on marshy soils. Gierth found Early Rose to be most affected by wet, and Anderssen the best cropper, and also to have the highest percentage of starch. Emmel notes that the best yield is produced when whole large seed is employed, and when the eyes are downwards. A. Leydhecker states that sets containing only the eyes from the end produce better crops than those sets which include only the side eyes.

E. W. P.

**Potato Culture.** By GURADZE-KOTTULIN and others (*Bied. Centr.*, 1883, 625—630).—The author gives an account of experiments in culture on a large scale. The field was of 31 morgen of marly clay on limestone, and had been manured the preceding autumn with 150 centners per morgen of stable manure. In the middle of April 16 well-chosen sorts of potatoes were sown, the ground kept carefully cleared of weeds, and the crop harvested in October, with the results given in Table I (p. 484).

A similar set of experiments were made by Sattig and Holdefleiss with 23 varieties, the soil being a mild loam. The crops yielded the number of centners per morgen given in Table II (p. 484).

Champions and Early Rose were all sound; the others were more or less attacked by disease.

Jacobs at Siernki made some few experiments in a field planted with rye the previous year, in good state, and which was manured again with 140 cntr. cow manure, 1 cntr. Chili saltpetre, 1 cntr.

TABLE I.

	Centner per morgen.	Per cent. diseased.		Centner per morgen.	Per cent. diseased.
Aurora .....	63·60	5·65	Own growing .....	84·50	2·44
Magnum Bonum ...	77·74	2·30	Late Rose .....	111·17	1·60
Grampian .....	29·48	16·60	Flourball .....	105·00	4·76
Champion .....	98·40	2·81	Richter's Emperor.	91·49	2·83
Alcohol .....	52·20	11·54	Garnet Chili .....	94·92	2·36
Farmer's Blush ....	65·00	5·48	Pomegranate .....	79·54	2·89
Kuzco .....	111·43	2·09	Gleason .....	93·51	2·43
Euphylos .....	84·13	13·59	Saxon bulb .....	64·90	8·65

TABLE II.

<i>A.—Manured with 180 Centners per Morgen of Stable Manure.</i>			
Champion .....	93·3	Snowflake .....	64·3
Early Rose .....	85·4	Alma .....	72·4
Garnet .....	73·0	Health .....	77·5
Onion Potato .....	63·3	Blanka .....	79·3
<i>B.—Manured with 100 Centners Chili Saltpetre per Morgen.</i>		Kutzko .....	73·2
Magnum Bonum .....	25·6	Chardon .....	81·4
Dabers .....	37·6	Farmer's Blush .....	82·6
Aurora .....	46·4	Lippe's Rose .....	100·1
Richter's Emperor .....	51·0	Griesenhäger .....	85·5
Late Rose .....	56·2	Alcohol .....	101·2
		Richter's long bearing .....	106·5
		Silesian .....	125·6
		Snow Rose .....	126·4
		Wabel Rose .....	171·3

Baker guano superphosphate per morgen; the seed averaged 10 cntr. per morgen, the crop in cntr. per morgen—

Haag's late Blue Rose	156·8	Improved Peach Blossom ..	146·4
Paulsen's Aurora....	156·4	Kopsel's Early White Rose.	141·3
Seed or Gleason ....	150·0	Early Goodrich .....	139·5

All of them withstood the disease well, but the Gleason and White Rose were the healthiest.

Vibrans reports experiments with various kinds on two descriptions of soil. The first field (see Table III, p. 485) was a good black strong loam, on which barley after beets had been grown the previous year. In December, 150 cntr. of stable manure per morgen was put in, in April ploughed for seed, and top dressed with 1 cntr. superphosphate and  $\frac{1}{2}$  cntr. saltpetre, harrowed and sown. The second field was high, dry, sandy with humus. The summer was hot and dry, favourable for the first, but unfavourable for the second.

The reports from various districts are all very favourable to the

TABLE III.

	Tubers.	Starch, per cent.	Starch, total.
<i>Field No. 1.</i>			
Emperor .....	169·00	16·4	27·72
Anderssen .....	134·30	17·9	24·04
Achilles.....	135·15	17·5	23·65
Ceres .....	149·20	15·4	22·98
Early Nassengrunder .....	138·90	16·4	22·78
Alcohol.....	134·40	16·6	22·31
Dabers .....	135·90	16·4	22·29
Champion .....	130·0	16·6	21·58
Trophine .....	117·20	18·4	21·57
Eos .....	114·75	17·9	20·64
Lippe's Rose.....	126·80	15·6	19·78
Reliable.....	129·56	15·1	19·55
Aurora .....	118·50	15·6	18·49
Farmer's Blush.....	133·00	12·8	17·02
Thusnelda.....	107·20	15·8	16·94
Blue Rose.....	128·0	13·0	16·64
Garnet Chili .....	103·8	15·8	16·39
Hertha .....	105·25	15·4	16·21
Paulsen No. 13 .....	138·00	11·7	16·15
<i>Field No. 2.</i>			
Eos .....	116·70	20·1	23·46
Imperator.....	124·25	17·1	21·25
Trophine .....	110·29	17·7	19·52
Lippe's Rose.....	106·50	17·5	18·54
Dabers .....	98·50	18·2	17·92
Thursnelda .....	100·47	16·6	16·67
Farmer's Blush .....	98·66	16·4	16·17
Blue Rose.....	100·10	14·5	14·50
Ceres .....	100·0	14·7	14·70

Champion, both for hardiness and resistance to disease, as well as being a large yielder.

A variety of suggestions are made to prevent the disease, such as trenching them up very high, planting them before winter 20—24 cm. deep, and in the next spring another row between the first at the depth of 8—12 cm. The deeply-planted were not frozen, and at harvest none of them were diseased, and but few of the spring sown.

Another plan is to wash the seed potatoes, dust them with flour sulphur and common chloride of lime till they acquire quite a thickish coating, then strew ashes on them.

J. F.

**Researches on Sugar-beet.** By H. HELLRIEGEL and others (*Bied. Centr.*, 1883, 842).—By “pitting” beet, an increase to the amount of 5 per cent. of its weight is obtained, due to absorbed moisture. The extraction process shows a smaller percentage of sugar than the polarisation method in the ratio of 95 : 100. The juice has a higher

sp. gr. than the root. Of two methods of obtaining the sugar from the juice, the digestion is better as regards yield than the extraction. In drawing samples, only good ones of medium size should be taken.

E. W. P.

**Heat Radiation from the Earth.** By J. TYNDALL (*Bied. Centr.*, 1883, 577—512).—A summary of experiments made by Tyndall, which originally appeared in *Nature*, the points chiefly dwelt on by the reviewer being the effect of invisible aqueous vapour in the atmosphere, the presence of which prevents the radiation of heat from the earth.

J. F.

**Micro-organisms in Soils.** By R. KOCH and P. MIGUEL (*Bied. Centr.*, 1883, 581—582).—From examinations of a large number of samples, Koch found that the superficial layers of soil were very rich in germs of bacteria, particularly in bacilli. Micrococci were only found in places which had not been cleansed from decaying matter; the latter perished on heating the samples, but the bacilli did not, being mostly in the condition of spores, and it appears probable that they are introduced by means of manures and household offal.

The quantity of micro-organisms diminishes very rapidly with increase of depth, so that at the distance of 1 metre from the surface the earth is very free from them. Miguel attempts to estimate the number present in 1 gram of soil taken from a depth of 0.20 metre from the surface, and found in three samples from—

Montsouris .....	700,000 organisms.
Gennevilliers, manured with liquid sewage .	870,000 „
Do. not so treated.....	900,000 „

The office of those minute organisms appears to be of great importance in the transformation of substances to forms suitable for plant-food.

J. F.

**Sterile Soil from California.** By A. VOELCKER (*Bied. Centr.*, 1883, 642).—The composition of this soil shows no deficiency in plant foods. The author thinks its sterility is due to its strongly alkaline reaction. To cold water it yields a half per cent. of mineral matter; sodium and potassium carbonates, sodium chloride, and nitrate. The author thinks nothing would make it fit for tillage but irrigating frequently to wash out the alkalis.

J. F.

**Theory of Manuring.** By P. WAGNER and others (*Bied. Centr.*, 1883, 798—818).—In a set of experiments already described, the results were untrustworthy, because of the small quantities of phosphate employed. In the present series, a larger quantity has been used, so that the differences of yield are more marked. Buckwheat, peas, oats, and vetches were the plants, and they were manured with precipitated calcium phosphate, and 21 per cent. citrate soluble phosphate (858 kilos. per hectare). Of these plants, vetches produced the highest increase above the blank plots, buckwheat least, and the albuminoids and phosphates of the peas and buckwheat were sensibly

raised. In 1882 experiments were made to estimate the value of calcium and potassium phosphates in comparison with the soluble phosphoric acid of superphosphates. Peas were grown in zinc boxes 25 cm. broad and 50 cm. deep, containing sandy soil; precipitated calcium phosphate was added at the rate of 150, 300, and 450 kilos. per hectare; and as gypsum is present in a "super," some plots were set apart for this substance. Nitrogen as sodium nitrate (50 kilos. N per hectare, 200 kilos. potash as potassium chloride, and 300 kilos. superphosphate) were the other manures. As the plants grew, the phosphates showed their influence by the darker green, broader leaves and stronger stem; at the same time the lower leaves became yellow and spotted prematurely. On weighing the yield, it was found that nitrogen had had no great effect by itself, producing only an increase of 1.5 per cent., and in conjunction with phosphate and potash, 5.3 per cent. Phosphates and potash were the most productive, but the increased ratio of phosphate to potash produced a corresponding fall in the ratio of straw to grain. The presence of the gypsum is considered to have been decidedly lowering to the yield, as one plot indicates; and the superphosphates, whether soluble in water or in "citrate," seemed to be equally valuable. The addition of phosphates was accompanied by a decreased yield and by an earlier yellowing of the leaves, with an increased percentage of phosphate in the plant itself. The addition of phosphates to nitrogen and potash raised the yield, but no increase in assimilated phosphoric acid; consequently, the author considers that the modern theory of the solvent action of nitrates on the phosphates in the soil must be modified. As stated above, the phosphates in the whole crop were increased, but further investigation showed that the increase was in the straw, whilst the percentage in the seed fell. The effect of the various manures on the albuminoids was only noticeable in those plants manured with superphosphate and nitrogen, when it was found that the albuminoids increased in the straw, but fell in the seed. A second series of experiments was also instituted in 1882, when the manures were 20 kilos. N per hectare, half as sodium nitrate, half as ammonium nitrate, 178.6 kilos. potash as chloride, and 40, 55, 70, 85, 100, 115, 130 kilos. phosphoric acid as fine superphosphate, precipitated phosphate, washed mineral "super," and potassium phosphate, also as much gypsum as corresponded to that in the washed super. The experiment is to be found in a previous communication. The results obtained are fully described, given in tabular form. It was found that so long as an increase of phosphate produces an increase of yield, the two increments bear a constant ratio to one another; but that after a certain point no further advantage is gained by increasing the quantity of manure. In the cases in question, the limit was 115 kilos. per hectare. When the various phosphates are compared with one another as regards their value, putting fine-grained super = 100, we find coarse-grained = 155, precipitated phosphate = 104, washed superphosphate = 80, and potassium phosphate = 103. If we allow that the gypsum present in the supers has a lowering effect in all cases, equal to that produced by gypsum alone, we may then calculate the effect of phosphates free from gypsum. This has been done, with the



remarkable result that all the various phosphates produced practically the same effects in the crops. Increase of phosphates in the ash of the plants was independent of the form in which the phosphate was applied, and the quantity in the ash increased with that applied. In like manner, the albuminoids were not affected by the form of combination, or by the quantity so long as there was an increase in the yield. To test the after-action of various phosphates, the soil, after removal of the peas, was planted with vetches and barley, and then it was found that, as before, the increase of yield was in direct proportion to the increase in manure, and that 115 kilos. phosphoric acid per hectare was the limit beyond which it was not advisable to pass: also as regards the manurial value of the different sorts, the results were identical with those of the previous season. The action of several other manures on plants has been described by the authors, as will be seen by reference to a previous number, where it is stated that potash has an injurious effect on the quality of potatoes; but the experiments of 1881 show that potassium chloride, after a strong manuring of phosphates, has no detrimental influence. E. W. P.

**Value of Various Nitrogenous Manures.** By M. MÄRCKER (*Bied. Centr.*, 1883, 584—590).—These experiments were made to verify those previously made by Seyffert, and were carried out by Albert. Chili saltpetre: The plants to which this manure was applied flourished during their entire growth. Ammonium sulphate had not so good an effect, the plants being far inferior to those of the first experiment. Horn-meal gave very satisfactory results at first, but a sort of second growth springing from the roots shortly before ripening weakened the plants. Blood-meal was slow in operation for three-fourths of the time, but then the plants made great progress; leather-meal gave very poor results; the fermented meal something better than the raw, but both unsatisfactory. Bone-meal, both raw and fermented, were very satisfactory, the latter causing a larger yield of straw; fermented blood-meal acted similarly to unfermented, but with greater energy. A plot which received no nitrogenous manure, but to which were added all mineral salts necessary for the growth of plants, made a very poor appearance, and the results in both straw and grain were unsatisfactory. The results show the sodium nitrate and horn-meal as the first, and the leather as the lowest in the scale of the manures tried.

The influence of these manures on the composition of the oats grown with them was very marked, the percentage of protein matter in that with leather, ammonium sulphate, and sodium nitrate being lowest, and with blood-meal and horn-meal yielding the highest. The time of harvesting also was influenced by the nature of the manures, those in which the nitrogen existed in an easily assimilable condition being first ready for cutting, but where it was present in an organic state as albumin, fibrin, &c., the harvest was some eight days later and the ripening irregular; the nitrogen in bones being in the form of gluten, was easily available.

Experiments were also made in order to test the reputed poisonous influence of cyanides on vegetation, but ammonium cyanide was

found not to be actually poisonous, and in certain cases its effects on oats were beneficial. The author thinks that farmers need not be too much afraid of purchasing superphosphates with a small percentage of cyanides. J. F.

**Examination of Aves Guano.** By M. MÄRCKER (*Bied. Centr.*, 1883, 582—584).—This deposit of guano, recently introduced to commerce, is found in the Aves Island, situate in the Carribean Sea off the coasts of Venezuela. The quantity is considerable, and according to the analyses of Märcker and others, it is one of those guano phosphates rich in phosphoric acid, but poor in nitrogen, the estimation of the former in different samples being 33·83; 25·18; 23·33; 33·12 per cent.; nitrogen, 0·21 to 0·28 per cent. It is described as being in good condition, a 5 kilo. sample which was examined containing powder 77·6 per cent.; grains 1—2 mm. 15·8; pieces over 2 mm., 6·6 per cent. J. F.

**Guano from Aves Island.** By E. GÜNTZ (*Dingl. polyt. J.*, 249, 187).—This island, off the coast of Venezuela, contains an enormous deposit of guano, which, when suitably prepared, has the following composition:—

Water .....	6·83 per cent.
Organic matter .....	7·03 „
Iron oxide .....	0·22 „
Alumina .....	0·36 „
Lime .....	42·62 „
Magnesia .....	2·03 „
Potash .....	0·14 „
Soda .....	1·44 „
Ammonium oxide .....	0·22 „
Phosphoric anhydride .....	33·12 „
Sulphuric anhydride .....	1·19 „
Carbonic „ .....	3·84 „
Nitric „ .....	traces „
Chlorine .....	1·07 „
Silica .....	0·18 „
Fluorine .....	0·00 „
Sand .....	0·17 „

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100·46

The total nitrogen in this prepared guano is 0·284 per cent.

J. T.

**Preparation of Poudrette.** By WEIGELT and C. ENGLER (*Bied. Centr.*, 1883, 819—821).—The contents of the cesspools are first disinfected by manganous chloride, and the liquid portion heated with lime, and boiled by steam, the resulting ammonia being collected in sulphuric acid. The liquid thus freed from ammonia then passes through a series of cisterns containing peat, which retains much of the potash and nitrogen in forms other than ammonia. The sediment

in the original liquor is dried, pressed, ground, and sold as poudrette, and contains 3—10 per cent.  $P_2O_5$ , 0.3—10 per cent.  $K_2O$ , 1—5 per cent. N.

Engler compares this process with those of Podewits and Lernur, and considers that the one described above (Buhl and Keller) is the most economical.

E. W. P.

**Some of the Changes which the Nitrogenous Matter in the Soil Experiences.** By R. WARINGTON (*Bied. Centr.*, 1883, 794—796).—The supply of nitrogen to the soil is kept up by the residue of the plant growing therein, the added nitrogenous manures applied, and that which is contained in the rain which falls, viz., 3—4 kilos. per hectare yearly, also a small quantity which is absorbed by the soil directly from the air as ammonia. The fertility of the soil is in a direct ratio to its richness in nitrogen, and that this law is correct is shown by the results obtained by the experiments on wheat and barley at Rothamsted; in both cases, the percentage of nitrogen and carbon is highest on those plots which received 7 tons farmyard manure per hectare, and which consequently produced the heaviest crops. Those plots which received ammonia salts were not rich in nitrogen, as much of it passed away into the drains as nitrates. Grasses and clover are the best retainers of nitrogen, whereas roots are the worst. The author likewise describes the nitrification process, and adduces figures from his analyses of the drainage waters in support of the theory.

E. W. P.

**Inferior Manures.** By STUTZER and others (*Bied. Centr.*, 1883, 590—592).—The authors notice certain manures sold principally in the vicinity of Cologne, which are of inferior composition, one in particular, called a siliceous poudrette, contained soluble phosphoric acid, none; total phosphoric acid, 0.2; nitrogen, 0.3; sand and clay, 82.8; silicic acid, 11.1; the selling price being 6 marks per centner, and the valuation 33 pfennige or  $\frac{1}{3}$  mark.

J. F.

**Continuous Cultivation without Stable Manure, employing Artificial Manures.** By D'AVENE (*Bied. Centr.*, 1883, 643).—This cultivation has been continued at Montoir (Loire and Cher) for 14 years with great success. The land in harvest is manured with 500 kilos. superphosphate, and in spring with 500 kilos. of special St. Gobain manure, or other equal to it. The accounts show a balance to profit.

J. F.

**Manuring of Tobacco.** By J. NESSLER (*Bied. Centr.*, 1883, 642).—Tobacco requires much potash in manure used in its cultivation, from one hectare yielding 33 centners it withdraws 75 to 100 kilos. potash; the potash cannot be applied in the form of chloride, as that yields a badly burning tobacco, so do other chlorides. Sulphates and nitrates, on the contrary, give a quick burning leaf; the best results have followed the application of 150 to 200 kilos. per hectare in suitable form. Stable manure should be cautiously used; phosphates are not of much use, but nitrogen should be used freely. Wool-dust would be a very good manure if its nitrogen was of quicker assimila-

tion; if used in a compost it should do well. Tobacco requires moisture and a loose humous soil: stable manure containing chlorides should be used early, and probably would do better if applied to the crop grown immediately previous to the tobacco. J. F.

**Sodium Nitrate and Ammonium Sulphate as Manures for Beets.** By P. P. DEHÉRAIN (*Bied. Centr.*, 1883, 593—594).—It may not be important, on some soils, whether nitrogen be applied in either of those forms, but the author has found a great difference in the results of their application on his experimental field at Grignon, a light soil containing lime, the ammonium salt having a very injurious effect on the roots if the soil did not possess sufficient organic constituents, some plots which were strongly manured with ammonium sulphate having had to be resown. He also found that the use of too strong a dose of the nitrate had not the effect of increasing the yield in proportion. In one experiment, in 1877, 400 kilos. per hectare produced 36,900 kilos. of roots, testing 17.4 per cent. of sugar; whilst 1,220 kilos. per hectare yielded but 29,800 kilos. of 12.7 per cent. sugar.

These results differ so much from a similar series of experiments made by Märcker, that the editor suggests there may be some conditions attached to the experiments which have escaped notice.

J. F.

**Stassfurt Salts as Absorbents in Stables.** By M. MÄRCKER (*Bied. Centr.*, 1883, 598—599).—The use of potash salts in stables for the purpose of absorbing and fixing ammoniacal exhalations is strongly recommended, but the author advises care in their selection, as those which contain much chlorides are less suitable, being very deliquescent and unpleasant to manage. Of the four cheaper salts: carnallite, kainite, polyhallite, and krugite, the first contains 24.3 per cent. of potassium chloride and 31.0 of magnesium chloride; it is therefore least suitable of all. Kainite containing 17 per cent. magnesium chloride can be used, but the author recommends krugite containing 20 per cent. potassium sulphate, and nearly 34 per cent. calcium sulphate, as the most useful for the purpose. J. F.

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## Analytical Chemistry.

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**On Desiccators.** By E. FLEISCHER (*Anal. Zeitschr.*, **23**, 33—35).  
—It is generally assumed that the air contained in a desiccator, after exposure for a few hours to the desiccating substance, is perfectly devoid of moisture. The author has made some experiments with a Lambrecht's hygrometer, and finds that whilst sulphuric acid after 35 minutes left but 30 per cent. of the original amount of moisture, after 1 hour 18 per cent., and after 105 minutes none at all, calcium chloride after 2 hours left 31 per cent., after 4 hours 25 per cent., and

after 6 hours 21 per cent. of moisture. The author therefore condemns the use of calcium chloride as a drying substance for desiccators.

O. H.

**Detection of Chlorine, Bromine, and Iodine.** By F. JONES (*Chem. News*, **48**, 296).—With regard to Vortmann's process for the separation of chlorine, bromine, and iodine (*Abstr.*, 1883, 119, 1167), the author has introduced a simple plan of utilising the same principle.

A small quantity of the substance to be tested is put in a test-tube along with some manganese dioxide and a little water. One drop only of dilute sulphuric acid (1 in 10 of water) is added; a brown tinge indicates iodine; boil until violet vapours cease to appear, and repeat the treatment with one drop of acid, and boiling until no more iodine vapour appears. Now add 2 c.c. of the dilute sulphuric acid and boil; bromine, if present, will be evolved. Repeat treatment with 1 c.c. of acid and boiling until all the bromine is expelled. Allow residue to cool completely, then mix with an equal volume of concentrated sulphuric acid and warm; if chlorine is present, it will be evolved.

D. A. L.

**Estimation of Sulphur in Pyrites.** By G. LUNGE and C. BODEWIG (*Chem. News*, **48**, 285).—Lunge has decided, from the results of experiment, that the nitric acid used in the aqua regia employed for dissolving pyrites should not exceed sp. gr. 1.420. Bodewig's process for "opening up" pyrites is as follows:—About 0.5 gram of substance is put into a small stoppered flask with 30 c.c. of water; 4 c.c. of bromine are then added, the stopper put in, and the flask shaken for five minutes. When the oxidation is complete, that is, when all the bromine is dissolved and all the pulverulent sulphur has disappeared, the liquid is washed into a shallow vessel, the greater part of the bromine allowed to evaporate, and the solution neutralised with ammonia, but not so as to form a permanent precipitate. It is then poured into excess of hot ammonia in a platinum capsule, and after digesting for 15 minutes over a flame, is filtered. The sulphuric acid is determined in the filtrate in the usual manner. Iron cannot be determined in the same sample, as some of the metal is always volatilised with the bromine.

D. A. L.

**Estimation of Thiosulphuric Acid.** By G. BRÜGELMANN (*Anal. Zeitschr.*, **23**, 24—25).—The proposed method consists in the oxidation of the thiosulphate by an excess of permanganate, and the estimation of the sulphate formed.

O. H.

*Note.*—The proposal is neither novel, nor has it any advantage over the ordinary volumetric methods.—O. H.

**Volumetric Determination of Ammonia.** By H. BECKURTS (*Dingl. polyt. J.*, **249**, 426).—The author states that phenolphthaleïn cannot be used as indicator for the titration of ammonia; he, however, advocates the use of phenacetolin.

D. B.

**Purification of Ammonium Fluoride.** By P. T. AUSTEN and F. A. WILBER (*Chem. News*, **48**, 274).—One of the most convenient

methods of determining silica in ores is to expel it as fluoride by means of ammonium fluoride and sulphuric acid or hydrofluoric acid alone; but neither pure hydrofluoric acid nor ammonium fluoride can be purchased. The authors have therefore introduced the following method for their purification. The ammonium fluoride or hydrofluoric acid is treated in a platinum dish with excess of strong ammonia; it is then filtered direct into the crucible containing the ore, through a folded filter previously washed with hydrofluoric acid, and supported in a ring of platinum wire. The liquid is acidified with sulphuric acid, evaporated to dryness, and ignited as usual.

D. A. L.

**Estimation of Ammonia in Vegetable Extracts.** By E. SCHULZE (*Anal. Zeitschr.*, **23**, 13—16).—It has been pointed out that Schlösing's method is not applicable in presence of asparagine, as this is decomposed with formation of ammonia. The author shows, however, that even after two days' contact with caustic lime only about 1 per cent. of the asparagine is decomposed, whilst ammonia salts yield during that time the entire amount of the ammonia contained in them, and that therefore even in fluids comparatively rich in asparagine the error is very small, and may safely be neglected.

O. H.

**Volumetric Determination of Combined Nitrous Acid.** By L. P. KINNICUTT and J. U. NEF (*Chem. News*, **48**, 274).—Finding the old method for the determination of nitrous acid in commercial samples of potassium and sodium nitrites unsatisfactory, the authors, after numerous experiments, devised the following modification of it. One part of the sample of nitrite is dissolved in at least 300 parts of water, and decinormal potassium permanganate is dropped in until a decided and permanent red colour is obtained; two or three drops of dilute sulphuric acid are then added, and immediately afterwards an excess of the permanganate solution. The liquid is made strongly acid with sulphuric acid, heated to boiling, and the excess of permanganate titrated with decinormal oxalic acid. Concordant results have been obtained by this method. The volumetric method for the determination of sulphites has been studied, but the results are not satisfactory either by the method described above or by iron alum and permanganate.

D. A. L.

**Ammonium Ferrous Sulphate as a Reagent for Nitric Acid.** By P. T. AUSTEN and J. C. CHAMBERLAIN (*Amer. Chem. J.*, **5**, 209).—As solutions of this salt are quite fit for use after standing for three months in a closed bottle, or for three weeks in a loosely-covered beaker, the authors recommend it for use in place of ferrous sulphate. Addition of about 2 per cent. of sulphuric acid improves its keeping powers. It is quite as delicate a test as ferrous sulphate.

A. J. G.

**Estimation of Phosphoric Acid as Magnesium Pyrophosphate, and the Influence of Reagents employed in separating the Acid from Bases.** By D. LINDO (*Chem. News*, **48**, 217—221; 230—231; and 239—243).—Pure microcosmic salt is employed in this investigation. After crushing and pressing between filter-papers,

it can be preserved in well-ground stoppered bottles for some time without change, although in time it loses weight.

In order to vary the tests, the pure salt was employed in different conditions, and test-solutions of various strengths were used thus:—Magnesia mixture containing per c.c.—(1) 0·0156 gram  $\text{MgCl}_2$ , 0·0825  $\text{NH}_4\text{Cl}$ , 0·0194  $\text{NH}_3$ ; (2) 0·0312  $\text{MgCl}_2$ , 0·1650  $\text{NH}_4\text{Cl}$ , 0·0127  $\text{NH}_3$ ; (3) same as (1) without  $\text{NH}_3$ . Dilute ammonia containing—(1) 6·34, (2) 2·52, (3) 1·20, (4) 11·54  $\text{NH}_3$  per cent.

Gooch's method of filtration is employed, the perforated crucible being provided with a plain one to act as a jacket. 500 c.c. of solution only were made at a time, and contained 7·5318 grams of microcosmic salt. For test experiments, 25 c.c. of this solution diluted with 75 c.c. water was precipitated with 12 c.c. of magnesia mixture (1), 10 c.c. of ammonia (1) added when the precipitate had settled, and the precipitate was washed with 200 (c.c.) of ammonia (3). Modified test experiments had the 10 c.c. of ammonia (1) added before instead of after precipitation; this is not to be recommended. Over 490 experiments have been made, and the author's conclusions, with some average results, are given below.

Experiments with *solid salt method* yielded accurate results. *Moderate heat* ( $60^\circ$ ) does not affect the accuracy of the results. *Large excess of magnesia mixture added gradually* never does harm, except in cases mentioned below, and is even necessary in presence of ammonium chloride, oxalate, and citrate, but even moderate excess *added all at once* causes high results, thus:— $\text{P}_2\text{O}_5$  per cent. found = 100·15 with 33 magnesia mixture (1) added gradually, 100·37 with 15 c.c. magnesia mixture (1) added all at once, and 100·10 in tests. The best *method of adding the magnesia mixture* is from a burette, a drop per second, with constant stirring. When *concentrated solutions* are precipitated, low results are obtained with magnesia mixture (1); this is owing to the ammonia present, as accurate results are obtained with mixture (3).

12 c.c. Mg. mix. (1).	Test.	12 c.c. Mg. mix. (3).	Test.	
99·86	100·12	100·02	99·98	$\text{P}_2\text{O}_5$ per cent.

With *neutral magnesia mixture* (3), the precipitation is not complete until the ammonia is added, which should be dilute (No. 3 solution), and should be run in by drops, stirring constantly. The precipitate is highly crystalline and easily washed; the results are accurate. *Precipitation in presence of excess of free ammonia* gives rise to low results; thus, when a solution was precipitated containing 85 c.c. of ammonia (4), 99·63 per cent was obtained, the tests averaging 100·04. This is probably due to the fact that the precipitate being bulky, amorphous, and difficult to wash, the washing solution dissolves more of it than in the case of crystalline precipitates. The precipitate is crystalline in presence of ammonium citrate, oxalate, or chloride (in large quantities), even when there is much free ammonia.



With regard to the *solubility of the precipitate in dilute ammonia*, no measureable difference has been detected between the solubility of the highly crystalline precipitates and that of the more bulky precipitates obtained in the ordinary test experiments. By a series of experiments it was found that precipitates washed with 200 c.c. ammonia (2) gave an average 100·04, whilst others washed with 600 c.c. gave 99·62. The difference, 0·42 per cent., represents the solvent action of 400 c.c. of ammonia (2), which would amount to 0·0063 gram of  $\text{Mg}_2\text{P}_2\text{O}_7$  per 3 litres of this solution. By direct quantitative experiments 3 litres of ammonia (2) washings gave an average of 0·0068  $\text{Mg}_2\text{P}_2\text{O}_7$ . From similar observations with solution (3), the numbers 0·0086 gram calculated, 0·009 gram found, were obtained. Therefore, in washing with ammonia (2) 0·0002, and with ammonia (3) 0·0003 must be added to the weight of the precipitate for every 100 c.c. employed. *Precipitation in the presence of ammonium chloride, oxalate, and citrate* is generally productive of low results, and that this is not wholly due to the solvent action of these salts on the precipitate is evident from the fact that the quantity of magnesia mixture required to counteract the solvent action of a given quantity of oxalate or citrate will not, if used in excess, precipitate all the phosphoric acid in presence of a similar quantity of oxalate or citrate, the volumes of the solutions being the same in both cases. It is probable, therefore, these reagents exert an action which impedes the formation of ammonium-magnesium phosphate, as will be observed by comparing some of the results in the tables (p. 496), which illustrates the effect exerted by these salts on the results obtained. When citric acid is employed, it is necessary to ignite the precipitate strongly to get rid of the carbon; this causes a somewhat greater loss in weight than when ignited in the usual way.

There is no evidence to support the idea that excess of magnesia mixture throws down magnesium oxalate or citrate, and therefore gives high results.

The *solvent action of these ammonium salts* on the precipitate is seen in the next table, along with the effect of using excess of magnesia mixture, which retards or even stops this solvent action.

Washing with solution containing 6 grms. $\text{NH}_4\text{Cl}$ .	Washing with do. and 20 c.c. Mg. mix. (2).	Tests.	Washing with solution containing 1 grm. $\text{NH}_4\text{Ox}$ .	Washing with do. and 20 c.c. Mg. mix. (2).	Tests.	Washing with solution containing 2 grms. $\text{Cl}(\text{HO})_3$ .	Washing with do. and 20 c.c. Mg. mix. (1).	Tests.
98·62	100·08	100·06	96·96	100·02	99·99	92·67	99·96	100·01

Ammonium sulphate gives rise to slightly high results; so that if reprecipitation is necessary accurate results are required in presence of this salt. Phosphoric acid can be separated by the oxalic method quite as accurately as by the molybdic method, even in the presence of aluminium and iron, provided the simple but necessary

2 grams $\text{NH}_4\text{Cl}$ . 12 c.c. Mg. mix.	Test. 1 gram $\text{NH}_4\text{Cl}$ . 12 c.c. Mg. mix.	0.25 gram $\text{NH}_4\text{Ox}$ . 12 c.c. Mg. mix.	Modified tests.	0.5 gram $\text{NH}_4\text{Ox}$ . 15 c.c. Mg. mix. (1). 25 c.c. of Mg. mix. (2).	0.5 gram $\text{NH}_4\text{Ox}$ . 15 c.c. Mg. mix. (1). 50 c.c. Mg. mix. (2).	Tests.
99.93	100.12	99.31	99.79	100.04	99.89	100.07

1 gram $\text{NH}_4\text{Ox}$ . 33 c.c. Mg. mix.	1 gram $\text{NH}_4\text{Cl}$ . 1 gram $\text{NH}_4\text{Ox}$ . 12 c.c. Mg. mix. (1).	Modified tests.	1 gram $\text{Ci}(\text{HO})_3$ . 12 c.c. Mg. mix. (1).	0.5 gram $\text{Ci}(\text{HO})_3$ . 12 c.c. Mg. mix. (1).	Modified tests.	2 grams $\text{Ci}(\text{HO})_3$ . 15 c.c. mix. (1).	2 grams $\text{Ci}(\text{HO})_3$ . 33 c.c. Mg. mix. (1).	Modified tests.
99.52	99.16	100.07	99.32	99.21	99.84	All corrected for loss by strong ignition (see p. 495).		
						98.39	99.38	99.83

1 gram $\text{Ci}(\text{HO})_3$ . 33 c.c. Mg. mix. (1).	1 gram $\text{Ci}(\text{HO})_3$ . 2 grams $\text{NH}_4\text{Cl}$ . 0.25 c.c. $\text{NH}_4\text{Ox}$ . 33 c.c. Mg. mix. (1).	Modified test corrected for blast.	2 grams $\text{Ci}(\text{HO})_3$ . 15 c.c. Mg. mix. (1). 25 c.c. Mg. mix. (2).	2 grams $\text{Ci}(\text{HO})_3$ . 15 c.c. Mg. mix. (1). 50 c.c. Mg. mix. (2).	Tests corrected for blast.
99.48	99.28	99.79	99.72	99.88	100.00

precautions indicated above are taken. Use only moderate excess of ammonium oxalate for precipitating the lime; use citric acid freely in presence of metallic oxides; precipitate with an excess of weak magnesia mixture added in the manner recommended, and when the precipitate is settled a large quantity of stronger magnesia mixture should be dropped in, &c.

In mixing citric acid solutions of ferric chloride with ammonia, the ammonia should always be added, as is generally done, after the citric acid and iron, for by doing the reverse the author obtained a precipitate deeply stained with ferric oxide in the subsequent precipitation of ammonium magnesium phosphate.

D. A. L.

**Separation of Strontium from Calcium.** By M. D. SIDERSKY (*Chem. News*, 48, 296).—The method is based on the fact that when a mixture of ammonium oxalate and sulphate is added to a solution containing strontium and calcium, all the strontium is precipitated as sulphate, whilst the calcium is found as oxalate, or its precipitation may be prevented altogether by acidifying the solution with hydrochloric acid. It is applied in the following manner:—Iron, alumina, &c., having been removed, filtered off, &c., the solution is acidified with hydrochloric acid, and precipitated by a solution containing per litre 200 grams of ammonium sulphate and 30 grams of oxalate. The strontium sulphate is filtered off, and the calcium is precipitated as oxalate by supersaturating the filtrate with ammonia. Satisfactory results have been obtained.

D. A. L.

**Qualitative and Quantitative Separation of Bismuth from Copper.** By J. Löwe (*Chem. News*, 45, 296).—In a previous communication, it was shown that bismuth and copper were precipitated from their solutions by potash and soda in the presence of glycerol, but that they were redissolved by excess of the precipitant. In this alkaline solution both are reduced by glucose at a boiling heat, the copper to red oxide, the bismuth to finely-divided metal, but in the cold or at a gentle heat the copper only is reduced after several hours, whilst the bismuth in solution remains unchanged, and even after several days only small quantities of the metal are deposited. This difference of behaviour is applied in the following manner for analytical purposes.

A moderately concentrated and slightly acid solution of the nitrates of the metals in question is mixed with a measured volume of soda until a precipitate forms and the liquid is alkaline; twice this volume of soda is now added, and pure glycerol stirred in until the precipitate is redissolved and the liquid clear. This solution is now mixed with a solution of glucose (1 in 6 or 8 of water) in quantity sufficient to make the sugar equal to three or four times the joint weight of the metals. The beaker is now covered over and left in a cool dark place for eight to ten hours, when the liquid will have lost its blue colour, and all the copper will be deposited as red oxide, from which the supernatant liquid is separated. The copper oxide is washed first with water containing glycerol and soda, collected on a weighed filter, well washed with water, dried at 100°, and weighed. The alkaline liquid

from the copper oxide is boiled in a porcelain capsule, stirring gently, for a short time, and when cool the metallic bismuth is filtered on a weighed filter, having been previously washed with water containing soda; it is then washed, dried, &c., in the same way as the copper. The operations with the finely-divided bismuth should be conducted as quickly as possible.

D. A. L.

**Analysis of Stannate of Soda.** By P. T. AUSTEN (*Amer. Chem. J.*, 5, 210—211).—The amount of stannic acid in this salt is usually determined by adding sulphuric acid to the hot solution until it becomes faintly acid; the results so obtained are good, but the gelatinous precipitate is very troublesome to wash. By adding strong nitric acid in excess and boiling, the author finds that the tin is completely precipitated as metastannic acid, and is much more readily washed and filtered than that precipitated in the usual manner.

A. J. G.

**Brucine a Test for Tin.** By E. R. DRYER (*Chem. News*, 48, 257).—Dissolve 0.1 gram of crystallised brucine in 1 c.c. pure nitric acid, add 50 c.c. water, heat to boiling, and cool. This solution gives a purple coloration with solutions containing stannous chloride. Neither zinc chloride, nor nascent hydrogen, nor organic matter, interferes with the reaction, but ammonium sulphide and sodium hyposulphite act like stannous chloride. To test for tin, dissolve the mixed sulphides of antimony and tin, obtained in the ordinary analytical separation, in hydrochloric acid, evaporate, dilute with water, and place a strip of platinum and a strip of zinc in the solution and in contact for several hours; metallic antimony is deposited on the platinum, whilst stannous chloride remains in solution, and can be tested for with a few drops of the brucine reagent. A distinct colour has been obtained with a drop containing only 0.0000025 gram of stannous chloride, whilst a drop containing 0.00002 gram gave a barely perceptible cloudiness with mercuric chloride. The reagent must not be too dilute, or the colour will be pale and indistinct; neither must it be used in excess, for then dirty green is produced instead of purple. The author finds this test for tin more delicate, more striking, and more convenient than the mercuric chloride test.

D. A. L.

**Separation of Cobalt from Nickel.** By J. CLARK (*Chem. News*, 48, 262—263).—The author has modified Dirvell's process (*Abstr.*, 1880, 287), the following being the chief points:—Instead of micro-cosmic salt, ammonium phosphate is found most suitable for precipitating the cobalt; sodium phosphate may be used, but large excess is necessary, whilst only a small amount of ammonium phosphate over that required for precipitating the cobalt, need be employed. Also it is not necessary to use ammonium carbonate or acetate, for ammonium chloride or sulphate, or nitrate, will do as well as the latter, and better than the carbonate. The following is the process:—In ores, the cobalt and nickel are precipitated as sulphides in an acetic acid solution, great care being taken to eliminate manganese, which would

interfere with the correct estimation of the cobalt. The mixed sulphides are ignited, weighed, and dissolved in nitro-hydrochloric acid. The solution containing the two metals is mixed with ammonium phosphate (about five times the weight of the combined cobalt and nickel) and with about 5 parts of the hydrochloric acid for every part of the ammonium salt, the mixture is boiled, the vessel removed from the flame, and while still hot ammonia is added in small quantities at a time until the precipitate, at first formed, is redissolved. The solution is then stirred vigorously, when the fine purple crystalline ammonium cobalt-phosphate separates out; 10 drops of ammonia are added, and the beaker placed on a water-bath for a few minutes. As soon as the precipitate settles, it is filtered, &c., and weighed as cobalt pyrophosphate. The filtrate is a clear blue, and probably contains a small quantity of cobalt, it is therefore heated at  $100^{\circ}$ , until the nickel begins to come down. If there is cobalt the precipitate will be reddish, if not it will be green. The precipitate is dissolved in hydrochloric acid, and the cobalt determined in the manner described. The nickel is precipitated as sulphide, and weighed as oxide. Very good results have been obtained, and the process is approved of by several chemists. The metals may be present as nitrates, chlorides, or sulphates, and nitric or sulphuric acid may be used instead of hydrochloric.

D. A. L.

**Volumetric Determination of Manganese.** By G. C. STONE (*Chem. News*, 48, 273).—This paper is a reply to Macintosh's criticisms (this vol., 220) on the existence of a precipitate of the composition  $10\text{MnO}_2, \text{MnO}$ . The author points out that his process referred to the analysis of spiegeleisen, and that Macintosh ignores the probable influence of the hydrocarbons derived from the carbon in the spiegel. The author's method of analysis is: 0.5 gram of spiegel is dissolved by boiling in 40 c.c. nitric acid (1.42 sp. gr.), excess of potassium chlorate gradually added, the whole cooled, filtered through asbestos, and the precipitate washed. The precipitate and asbestos are added to excess of standard oxalic acid (8 to 8.5 grams per litre), sulphuric acid is poured in, the whole heated until dissolved, and the excess of oxalic acid titrated by permanganate (3 grams per litre). The results were in favour of the formula  $10\text{MnO}_2, \text{MnO}$ , as against  $\text{MnO}_2$ . Similar experiments show that the author's modification (see above) of Williams's method is better than the original. The author has not found any appreciable difference in the results, whether he works with his method of adding the chlorate or that recommended by Macintosh (*loc. cit.*). Neither does he recognise the importance of the cooling for some time after the precipitation with chlorate. Finally, he considers that his present experiments confirm his original conclusions with regard to the spiegeleisen precipitate.

D. A. L.

**Titration of Organic Matter in Potable Waters, by Means of Permanganate.** By A. R. LEEDS (*Anal. Zeitschr.*, 23, 17–21).—A few experiments are quoted, showing that on boiling standard permanganate in alkaline solution (Schulze-Trommsdorf's method)

the permanganate undergoes an appreciable amount of decomposition, thus yielding indications of organic matter, which are beyond the amounts present, whilst no such decomposition takes place on boiling an acid solution (Kubel-Tieman's method). The latter mode of procedure is therefore recommended. O. H.

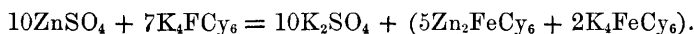
**Investigation of Petroleum.** By F. BEILSTEIN (*Dingl. polyt. J.*, 250, 169).—Although the forms of apparatus invented by Abel, Engler, and others, for the purpose of ascertaining the flashing point of petroleum, give concordant results in trained hands, it is necessary in constructing them to adhere strictly to the same form of apparatus, as a slight deviation influences the results to a considerable extent. The results obtained with the apparatus introduced by Liebermann and Stoddard vary with the size of the apparatus and the mode of applying the igniting flame.

The author recommends the following form of apparatus. It consists of a glass cylinder 35 mm. in diameter and 175 mm. long, marked at a distance of 70 and 140 mm. from the bottom with a divisional line. The cylinder is filled to the bottom line with oil. Air is admitted through a small brass tube, which dips into the oil and is bent round the cylinder, its end being provided with a rose-jet. The bulb of the thermometer is immersed into the middle of the oil column. At intervals of every degree of temperature air is forced through the liquid at a rate sufficient to raise the foam to the top line, a light being applied at the same time to test the flashing point. The results are said to be 5° higher than those obtained with Engler's apparatus.

The author states that the flashing point of petroleum determines only its degree of inflammability, and not the burning properties of the oil. This can be tested only by subjecting the oil to fractional distillation. American petroleum should not yield more than 5 per cent. of distillate under 150°, and not more than 15 per cent. of heavy oil boiling above 270°. Caucasian petroleum contains the hydrogen addition-products,  $C_nH_{2n}$ , of the aromatic hydrocarbons: hence it has a higher density and greater illuminating power than American petroleum. D. B.

**Estimation of Sulphur in Organic Compounds.** By E. H. KEISER (*Amer. Chem. J.*, 5, 207—208).—The author obtains very accurate results by the following modification of Liebig's method for the estimation of sulphur in non-volatile compounds:—10 grams of potash is fused in a silver crucible, allowed to cool, the weighed substance (0.1—0.3 gram) added, the crucible heated until the contents have become thoroughly mixed; 1 gram of potassium nitrate is then added, and the heating continued until the mass has become clear. When cold the fused mass is dissolved in water, neutralised with hydrochloric acid, and diluted to  $\frac{3}{4}$ —1 litre, when all silver taken up from the crucible during the fusion is precipitated. This is filtered off, and the sulphuric acid in the filtrate determined in the usual way, by precipitation with barium chloride. The barium sulphate does not need reprecipitation. A. J. G.

**Potassium Ferrocyanide Production.** By K. ZULKOWSKY (*Dingl. polyt. J.*, **249**, 168—178).—The author gives a rapid and adequate method for the examination of the fused product in making ferrocyanide. As is well known, the ferrocyanide is first produced on the addition of water to the fused mass; in the solution obtained, other cyanides are present in small quantity along with sulphides, potassium carbonate, &c. In a manufactory, the author found a method in use for estimating ferrocyanide which has not before been published; it is founded on the known reaction between potassium ferrocyanide and a soluble zinc salt. The author has investigated the process and devised a satisfactory method of working it. A standard zinc sulphate solution is acidified with dilute sulphuric acid, and the filtered ferrocyanide is run in from a burette until a slight excess has been added; this is ascertained by carefully placing a drop of the mixed solutions on filter-paper, and then placing near a drop of dilute ferric chloride solution, care being taken that no portion of the zinc precipitate is touched with the chloride solution. Adding the zinc solution to the potassium ferrocyanide is not satisfactory. Too much sulphuric acid diminishes somewhat the amount of ferrocyanide required for a given amount of zinc solution. When the acidified zinc solution is heated to boiling variations in the amount of sulphuric acid no longer have any influence, the zinc precipitate is pulverulent, so that more care is required in applying the ferric chloride. The following equation represents the process:—



**Thiocyanates.**—Although a portion of the thiocyanate in the solution is probably formed during the lixiviation, the amount found is usually returned as being present in the fused product. To estimate this, a measured volume of the solution is treated with a large excess of aqueous sulphurous acid, and allowed to stand about a day. Sulphur and a brown mass, produced by the decomposition of hydrocyanic acid, separate out. The acid liquid is neutralised with zinc oxide, and zinc sulphate is added to precipitate the ferrocyanide. The filtrate is concentrated, treated with aqueous sulphurous acid and sufficient copper sulphate to produce a distinctly green colour. The white precipitate is heated with sulphur in a current of hydrogen.

J. T.

**Wine Examination.** (*Dingl. polyt. J.*, **249**, 311—312.)—According to S. Kilicsan, not only young wines but old and well kept wines contain ammonia; in six samples from 0.0057—0.0113 per cent. was found. Formic acid can often be detected in the distillate from unsulphured wines. Since the precipitate produced in a wine distillate by silver nitrate contains carbon, probably from the presence of organic acids, Kilicsan considers Wartha's process for the detection of sulphurous acid in wines to be untrustworthy.

J. Nessler and M. Barth give a method for estimating free tartaric acid in wine as an improvement of the original Berthelot-Fleurieu's process. 50 c.c. of wine are evaporated to thin syrup, this is well shaken with 70 c.c. of 96 per cent. alcohol, and allowed to stand four hours in

a cool place, to permit the tartrate to settle out. The precipitate is separated, and its acidity reckoned as tartrate. The filtrate is freed from alcohol, and 0.5 c.c. of acidified 20 per cent. solution of potassium acetate is stirred into the syrupy residue, and the newly formed tartrate is estimated as before. But this method fails in case of wines strongly plastered, although negative values cannot be obtained, as are sometimes got by the older method.

For the estimation of sugar by Fehling's solution, the tannin must first be removed by lead acetate, the excess of lead being removed by sodium carbonate. Ordinary fully fermented wine usually contains under 0.1 per cent. sugar, and may be decolorised by a small quantity of animal charcoal; after rendering it alkaline with a little caustic alkali or carbonate, 5 c.c. is warmed with 2 c.c. Fehling, in a water-bath. If the blue colour completely disappears the wine contains over 0.2 per cent. sugar. If the blue colour persists 5 c.c. more wine may be added, and the warming repeated. In this way an approximation to the amount of sugar may be made.

J. T.

**Detection of the Colouring Matter of Campechy Wood in Wine.** By BONI (*Bied. Centr.*, 1883, 854).—Decompose with milk of lime, filter, dilute, add sulphuric acid until the liquid begins to appear red, then pour in absolute alcohol and filter. The addition of ammonium molybdate changes the colour into purple-red if the wine has been adulterated.

E. W. P.

**Detection of Artificial Colouring Matters in Wine.** By P. PASTROVITCH (*Bied. Centr.*, 1883, 865).—Magenta is not decolorised by manganese peroxide, but the juice of bilberries, elderberries, red and blue woods, cochineal, and orseille are all altered in colour; cochineal is decolorised, but the red in wines are changed to brown-yellow.

E. W. P.

**Sugar Analysis.** (*Dingl. polyt. J.*, 250, 133—136).—According to Vivien, it is difficult to estimate the glucose in sugar when the quantity is less than 0.1 per cent. The following colorimetric method is recommended:—10 grams of sugar are dissolved in 200 c.c. water, treated with 10 mgrms. glucose, and boiled. If after allowing the mixture to settle the supernatant fluid is decolorised, and a red precipitate formed, the sugar contains at least 0.1 per cent. of glucose. If no decolorisation occurs the change on raising the mixture to boiling is compared with ten solutions of glucose similarly treated, containing 1—9 mgrms. glucose. Zulkowsky states that the optical examination of a mixture of cane- and invert-sugar is adapted only to cases in which the quantity of invert-sugar predominates, as the specific rotatory power of this sugar is so small that the unavoidable errors of observation give rise to serious differences. Clerget's formula  $R = 100 (D + D^1) : 144 - 0.5t$ , recommended by Reichardt and Bittmann for the estimation of cane-sugar in molasses, &c., gives inaccurate results when the quantity of invert-sugar is large, as then the temperature must be taken into account both before and after inversion.

The values for the quantity of invert-sugar in 100 c.c. of solution



for various temperatures are based on the observations of Tuchschnied, who found that 17.21 grams of invert-sugar obtained from 16.35 grams of sucrose dissolved to 100 c.c., exert an optical action of  $-(44.16 - 0.506t)^{\circ}$  Soleil. Zulkowsky has accordingly calculated the quantities of invert-sugar, corresponding with  $1^{\circ}$  of saccharimeter for the temperatures of  $15-22^{\circ}$ . The following table illustrates the results obtained:—

Temperature observed.	Grams invert-sugar contained in 100 c.c. solution by the optical action of		
	$1^{\circ}$ Soleil.	$1^{\circ}$ Ventzke.	$1^{\circ}$ Wild.
15°	0.4706	0.7506	2.1676
16	0.4772	0.7612	2.1983
17	0.4839	0.7719	2.2292
17.5	0.4875	0.7776	2.2456
18	0.4910	0.7832	2.2616
19	0.4981	0.7945	2.2944
20	0.5056	0.8064	2.3287
21	0.5133	0.8187	2.3642
22	0.5210	0.8311	2.3992

For the determination of invert-sugar and cane-sugar, Zulkowsky first determines the amount of sucrose by polarisation, then the quantity of invert-sugar. His method is described in detail in the original paper. D. B.

**Clerget's Method of Sugar Analysis by Inversion.** By A. J. KING (*Chem. News*, 48, 229).—In using this method for determining the amount of cane-sugar in a mixture already containing invert-sugar, attention is called to the importance of taking the reading of the polariscope both before and after the inversion at the same temperature; for the rotatory power of invert-sugar varies with the temperature, a factor which should remain constant if the true value of the cane-sugar is to be found by this method (comp. *ibid.*, 45, 148). D. A. L.

**Estimation of Phenol in Commercial Carbohc Acid.** By KLEINERT (*Anal. Zeitschr.*, 23, 1—13).—The author has compared the results of estimating phenol by Koppeschaar's method (titration by means of standard bromine solution) and by fractional distillation. He finds that they in nowise agree, the bromine titration yielding figures which are far higher than the quantity of phenol which can be present. All samples which he examined yielded but a very small proportion of products volatile between  $150^{\circ}$  and  $200^{\circ}$ , phenol distilling between those temperatures. Between  $200^{\circ}$  and  $250^{\circ}$  the largest fractions are obtained, practically devoid of phenol, and yet giving copious bromine precipitates. Even at temperatures higher than  $250^{\circ}$  distillates are obtained, which give the bromine reaction, but do not show the well-known phenol indications with ferric chloride, hypo-

chlorite, or fir-wood and hydrochloric acid. Kleinert therefore concludes that Koppeschaar's method is not applicable for the valuation of commercial carbolic acid. O. H.

**Estimation of Tartaric Acid in Wine.** By R. KAYSER (*Anal. Zeitschr.*, **23**, 28—29).—For this purpose Berthelot's method, consisting in the separation of the acid in the form of acid potassium tartrate and titration of the latter with normal alkali, is usually employed; but in addition to other sources of error which have often been pointed out, this method involves the separation of the calcium present in the form of calcium tartrate, which, of course, is neutral to normal alkali. In a number of determinations of the lime contained in the precipitate, the error involved was found to vary from 0·2—0·6 per cent. of tartaric acid, and in several instances was larger than the total amount of tartaric acid calculated from the acidity only. The error is the greater the older the wine and the smaller the percentage of tartaric acid. The amount of lime has therefore to be determined, and an equivalent quantity of tartaric acid to be added to that found acidimetrically by Berthelot's method. O. H.

**Examination of Fats.** By E. VALENTA (*Dingl. polyt. J.*, **249**, 270—273).—The author has examined a series of fats by a method proposed by J. Köttstorfer, for the detection of foreign fats in butter. The fat to be examined, if necessary, is filtered whilst warm, and a weighed portion is saponified with standard alcoholic solution of potash. After warming on the water-bath about 15 minutes, the excess of potash is titrated by half normal hydrochloric acid, using phenolphthaleïn as indicator. Pure butter fat requires per gram about 227 mgrms. of potassium hydroxide for saponification, whilst many fats used for adulteration, such as suet, lard, bacon fat, mutton fat, rape oil, olive oil, oleomargarine, poppy oil, and walrus oil, require about 197—198 mgrms. The author has examined both animal and vegetable fats. Some of the results obtained tend to throw doubt on the suitability of the method for butter testing, whilst in other cases the nature of single fats can be ascertained, and adulteration can be detected quantitatively if somewhat considerable. The results obtained are given in tabular form. Palm-kernel oil with 247 mgrms., and cocoa-nut oil with 257—268 mgrms., are much higher than any others of the list, excepting cod-liver oil with 213 mgrms. Cocoa-nut oil contains not inconsiderable quantities of laurine and myristic acids, also small quantities of caprylic acid, &c. These acids contain much less carbon in the molecule than do palmitic, stearic, and oleic acids, hence the high saponifying value of this fat. Apricot-kernel oil, oil of sweet almonds, oil of bitter almonds, arachis oil, cotton-seed oil, olive oil, sesame oil, average 193 mgrms. Pumpkin-seed oil, oil-cake oil, rape oil (Hungarian product), average 188·1 mgrms. Rape oil, mustard-seed oil, and castor-oil average 177·1 mgrms. American bone-fat, goose-fat, pig-fat, average 191—196. J. T.

**Iodine in Cod-liver Oil.** By E. C. C. STANFORD (*Chem. News*, **48**, 233).—Various authorities have published results at various

times in which cod-liver oil is said to contain from 0·487 to 0·0295 per cent. of iodine, and in Garrod's *Materia Medica* it is stated to contain 0·06 per cent. If such were the case, cod-liver oil would be one of the richest sources of iodine, which the author considers improbable. Bird (*Pharm. J. Trans.* [2], 1, 546) published results of six analyses of cod-liver oils, four from Norway averaging 0·001355 per cent. iodine, and two from Newfoundland with 0·000993 per cent. The author has now made some determinations by a process which he has employed daily for many years in estimating small quantities of iodine, and by which  $\frac{1}{250000}$  part of iodine is easily detected and measured, and up to  $\frac{1}{100000}$  part accurately estimated. 5000 grains of oil are saponified with 1000 grains pure caustic soda, then carbonised in a porcelain crucible, the resulting charcoal is treated with water, and the solution made up to 5000 grains measure. 500 grains of this solution are treated with 100 grains measure of carbon bisulphide, and about three drops of nitrosulphuric acid—sulphuric acid, sp. gr. 1·843, saturated with gaseous nitrous anhydride—dropped in. The testings are performed in large even tubes, and the colour produced compared with graduated standard solutions of potassium iodide, treated in the same manner. The results of the analyses of several samples of cod-liver oil and some other substances are as follows:—

	Per cent. iodine.
Cod-liver oil, pale .....	0·000410
„ Norway .....	0·000434
„ Carr and Sons .....	0·000276
„ English .....	0·000138
„ Newfoundland .....	0·000315
Light brown cod-liver oil .....	0·000360
Cod liver, fresh .....	0·000817
*Cod-liver oil, dragées .....	0·056366
Oil vomited by the fulmar, a bird of St. Kilda .....	0·000095
†Fresh cod-fish, 0·00016 .....	dry = 0·000829
†Scotch herring, salted .....	0·00065
† „ brine .....	0·00012
Whale oil, cold drawn .....	0·00001
Bottlenose oil, cold drawn .....	0·00010
Seal oil, cold drawn .....	0·00005

To analyse kelp, 100 grains are treated twice with four ounces of hot water, the residue is washed, and the solution made up to 5000 grains; 500 grains of this are treated with carbon bisulphide, &c., as described above. In the actual testing, the author never operates on a solution containing more than one-tenth of a grain of iodine; for if this quantity is exceeded, the solution is diluted before testing. Sea-weeds or organic materials are first carbonised previous to being

\* Made of cod liver from which the oil is removed; for analysis 1000 grains were saponified with 200 grains of caustic soda.

† In these cases 5000 grains were treated with 500 grains of caustic soda. Other analyses were conducted as described above.

treated as described. Carbonising is preferable to burning to ash, because all the iodine is retained and the salts are easily extracted, whilst burning to ash causes loss of iodine and frequently leaves a fused mass. For testing the free iodine, carbon bisulphide is far preferable to starch, inasmuch as the latter is liable to change, is in many cases untrustworthy, and gives turbid solutions with the colour distributed throughout; whilst the former does not change, is quite trustworthy, the solutions are clear, and the colour is concentrated at the bottom of the tube. The author recovers the iodine from the bisulphide by means of zinc in the presence of water. D. A. L.

**Examination of Beeswax.** By HÜBL (*Dingl. polyt. J.*, **249**, 338—342).—Along with physical examination, F. Becker's saponifying test is of value. This test is given as Köttstorfer's butter test (see Abstr., p. 504). According to Becker, 1 gram beeswax requires 97 to 107 mgrm. potassium hydroxide for complete saponification. By mixing various waxy substances, impure beeswax can be made to give the same number. This difficulty can be overcome by ascertaining not only the total amount of potash required for complete saponification, but also that required to saturate the free acid (cerotic acid) present. Two numbers are thus obtained, which bear the constant relation of 1:3·7, as determined in about 20 samples of yellow wax. About 4 grams wax is treated with 20 c.c. neutral 95 per cent. alcohol, heated to fusion, and titrated with alcoholic potash solution, phenolphthalein being used as indicator. When the first number has been obtained, 20 c.c. potash solution are added, and the excess titrated with half normal hydrochloric acid. For the acid in 1 gram wax about 19 to 21 mgrm. KHO are required, and for the saponification 73 to 76 more are required. The proportion varies between 1:3·6 and 1:3·8, and the total potassium hydroxide used is 92 to 97 mgrm. The author designates the numbers thus obtained as acid number, ether number, and saponifying number respectively. Wax substitutes give very different values for these numbers, as the following average results show:—

Substance.	Acid number.	Ether number.	Saponifying number.	Proportion ether: acid.
Japan wax .....	20	200	220	10
Carnauba wax .....	4	75	79	19
Tallow .....	4	176	180	44
Stearic acid .....	195	0	195	0:195
Resin ..	110	1·6	112	0·015
Neutral substances ....	0	0	0	0
Paraffin.....				
Ceresine .....				
Yellow beeswax.....	20	75	95	3·75

Hence if the saponifying number falls below 92 with a proper proportion, the wax is adulterated with an inert substance (*i.e.*, paraffin). If the proportion be greater than 3·8, an addition of Japan or car-

nauba wax or tallow is probable. If the acid number be low, Japan wax is excluded, and of the remaining two the ether number will determine which has been used. If the proportion be below 3.6, stearic acid or resin has probably been added. It is also clear that the simultaneous presence of an active and an inactive substance may be detected by the figures obtained. The subject is being further investigated. J. T.

**Estimation of Urea.** By W. H. GREENE (*Compt. rend.*, **97**, 1141—1142).—A tube of 20—25 c.c. capacity, closed at one end and graduated, is sealed on to the upper part of a flask of about 50 c.c. capacity, with a side tubulus. The flask and tube are completely filled with sodium hypobromite solution, and the urine to be examined is slowly introduced into the middle of the flask by means of a graduated pipette with a narrow curved end. When the evolution of gas ceases, a funnel tube is attached by means of the tubulus, hypobromite solution is poured into it until the levels in the funnel tube and the graduated tube coincide, and the volume of the gas is read off. Instead of using the side tube, the apparatus, with the tubulus open, may be immersed in a vessel of water until the level of the water coincides with that of the hypobromite. As a control, a similar experiment may be made with a standard solution of urea.

C. H. B.

**Separation and Estimation of Digitalin, Digitalein, and Digitin.** By R. PALM (*Anal. Zeitschr.*, **23**, 22—23).—The German method of separating digitalin from the other alkaloids occurring in *Digitalis purpurea* is based on the precipitation of that alkaloid by means of tannin; the French method on the insolubility of digitalin and digitin in water, digitalein being readily soluble.

Both methods are troublesome and demand much time. The author extracts the powdered herb with water, filters the solution through animal charcoal until it is colourless, and precipitates the organic acids with neutral plumbic acetate. A solution of lead acetate and alcoholic ammonia is then added to the filtrate as long as a precipitate is produced. This contains all the alkaloids and is washed with water, and decomposed with hydrogen sulphide. The solution, separated from the precipitate, contains all the digitalein, the precipitate consisting of plumbic sulphide, digitalin, and digitin. The digitalin is extracted from the dried residue by chloroform, and digitin with alcohol.

O. H.

**Valuation of Indigo.** By C. H. WOLFF (*Anal. Zeitschr.*, **23**, 29—32).—The author has previously described (*Anal. Zeitschr.*, **17**, 310) a method of estimating the percentage of indigotin in commercial indigo by means of quantitative spectrum analysis, as introduced by Vierordt. He then employed a standard solution made from indigotin, which had been prepared by Trommsdorff. The artificial preparation of indigotin by Baeyer's process has now furnished the means of obtaining the colouring matter in a state of perfect purity, and Wolff has compared this with samples of indigotin pre-

pared by various manufacturers and also with commercial indigos, when the following results were obtained :—

Indigotin, Baeyer .....	100·00	per cent.
„ Trommsdorff .....	91·58	„
„ sublimated, Schuchardt ..	83·41	„
„ „ Wolff .....	82·45	„
„ Vierordt .....	81·95	„
„ crys. Schuchardt .....	79·08	„
Indigo, Java .....	72·42	„
„ Bengal, best .....	63·97	„
„ „ medium .....	60·47	„
„ „ third quality .....	20·94	„
„ Guatemala .....	50·70	„
„ Madras .....	23·10	„
„ Manilla .....	9·41	„

O. H.

## Technical Chemistry.

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**Antiseptic Action of Carbonic Anhydride.** By H. KOLBE (*J. pr. Chem.* [2], **28**, 61—62).—The author has pointed out that carbonic anhydride is an excellent means for preventing the putrefaction of meat (Abstr., 1883, 395). This was observed by Hermbstädt in 1791. H. B.

**Illuminating Gas and Gas Engines.** By F. FISCHER (*Dingl. polyt. J.*, **249**, 178—182).—A sample of Hanover gas, analysed by a method described, was found to contain

Benzene .....	0·69
Propylene .....	0·37
Acetylene .....	2·11
Methane .....	37·55
Hydrogen .....	46·27
Carbonic oxide .....	11·19
Carbonic anhydride .....	0·81
Oxygen .....	trace
Nitrogen .....	1·01

---

100·00

When this gas was used to drive a 6 horse-power Otto's gas engine, the waste gases were found to contain 6·0 to 7·7 per cent. of carbonic anhydride, and 9·9 per cent. of oxygen. When the engine was running without load, the waste gases contained 2·4 per cent. carbonic anhydride, and 17·2 per cent. oxygen. The temperature was about 400° C.

An engine driven by petroleum gas gave waste gases with 9·4 per cent. carbonic anhydride, and 5·1 per cent. oxygen; some little petroleum was carried over unconsumed. The temperature was 253° C. in this case, and when running light, the temperature was 130° C. with 6·0 per cent. carbonic anhydride, and 11·4 per cent. oxygen in the waste gas. Evidently the gas engine works with twice as much air as is necessary, and when running light, with three or four times as much. Hence much poorer gas can be employed by properly adjusting the amount of air supplied, and probably even generator gas may be used.

E. Grabau shows that the cost of steam driving per horse-power per hour varies from 3·4 to 8·1 pfennige, whilst the price of gas driving varies from 4·3 to 12·55 pfennige, according as gas varies from 3 to 14 pfennige per cubic metre. J. T.

**Retort Furnaces with Gaseous Fuel.** By F. FISCHER (*Dingl. polyt. J.*, 249, 346—350).—The author compares the working of three different systems in operation at the Hannover Gas Works. Samples of generator gas were taken from two of the furnaces, the Klönne and the Stettin, and for comparison the composition of gas from the Munich generator is also given on Table I. A sample from the third furnace (Liegel) could not be obtained.

TABLE I.

	Klönne.				Stettin.		Munich.			
	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
CO <sub>2</sub> ....	3·00	13·10	7·06	4·40	5·19	5·40	9·1	12·2	9·3	8·6
CO ....	29·99	16·39	27·43	30·21	28·19	27·76	19·8	17·4	20·4	20·6
CH <sub>4</sub> ....	—	1·06	1·22	0·44	—	—	—	—	—	—
H .....	7·63	16·18	15·56	16·65	2·58	3·98	13·9	14·0	9·8	15·0
N .....	59·38	53·27	48·73	48·30	64·04	62·86	57·2	56·4	60·5	55·8

In sample 1, the steam supply under the grate was somewhat weak; 2 was taken just after cleaning out the grate; 3, taken with grate somewhat slagged; 4, working well; 5 and 6, working well. In 7, 8, 9, and 10, no account appears to have been taken of methane. An average sample of the coke used, taken on the last day of the experiments, gave C 92·7, H 0·29, ash 4·95, O, N, S and loss 2·06 per cent. The Klönne and Liegel furnaces have a regenerative arrangement to heat the air before combustion, whilst the Stettin furnace is not so provided. The following table (p. 510) shows the composition of the waste gases, and an estimation of the relative efficiency of the furnaces.

The results marked with a (+) are when the furnace is working normally. For each 100 kilos. coal in the retorts the Klönne furnace requires 13 kilos. coke, the Liegel 15 kilos., and the Stettin 19 kilos.; whilst by ordinary grate firing 23 kilos. coke are necessary.



Furnace.	Composition of gases.				Temp. in chimney.	Loss of heat per kilo. coke.	Per cent. of total calorific value.
	CO <sub>2</sub> .	CO.	O.	N.			
Klönne ..... +	18·6	0	1·4	80·0	595°	2020 C.	26·9
	10·6	0	9·9	79·5	610	3340	44·4
Liegel ..... +	16·0	0	4·4	79·6	730	2700	36·0
	13·0	0	7·5	79·5	715	3200	42·6
Stettin ..... +	18·9	0	1·2	79·9	1160	4000	53·3
	16·1	0	4·4	79·5	1105	4300	57·3
	18·3	4·7	0	77·0	1220	4400	58·6
	8·6	0	12·0	79·4	900	6000	8·00

J. T.

**An Evaporation Experiment.** By F. FISCHER (*Dingl. polyt. J.*, **250**, 72—79).—The author gives a description of a comparative experiment made with a view to ascertain the evaporative power of coal and the variations in the composition of the flue gases. The boilers employed were of two constructions. In the one case, a German boiler was used, having a wide corrugated fire-tube inserted laterally; whilst as a comparison an ordinary Lancashire boiler with two smooth fire tubes was used. The heating surface in both cases amounted to 86 square meters, the area of the hearth of the English boiler being 2·8 square meters, and that of the German boiler 1·9 in the trials made July 5 and 6; and 2·4 square meters in those made August 3 and 4. The coal was obtained from the Saelzer and Neuack mine, and gave by analysis:—

C.	H.	N.	S.	O.	H <sub>2</sub> O.	Ash.
79·63	4·08	1·22	0·88	4·43	3·00	6·76

corresponding according to Dulong's formula to

$[8100 \times 79·63 + 28,800 \left(4·08 - \frac{4·43}{8}\right) + 2500 \times 0·88 - 600 \times 3] : 100$   
 = 7471 units of heat calculated on water of 20° as combustion product. The results of the experiments are summarised in the subjoined table (p. 511).

The widest differences in the composition of the gases at intervals of 60 minutes were obtained with the English boiler; this the author attributes to the difference in the dimensions of the fire tubes of the two boilers.

D. B.

**Contamination of the Atmosphere by Products of Respiration.** By J. T. H. HERMANS (*Dingl. polyt. J.*, **249**, 419—423).—It is a well known fact that men who live in crowded spaces are more readily subject to disturbances of health than other persons, and that supplies of fresh air improve the health and activity of such inhabitants. The author has made it his object to determine the causes of atmospheric contamination induced by the influence of respiration, and the work of the human skin.

*An Evaporation Experiment.*

	German boiler.				English boiler.	
	July 5.	July 6.	Aug. 3.	Aug. 4.	July 19.	July 20.
Duration of trial—minutes .....	620	715	600	705	600	720
Kilos. of water evaporated .....	23,174	25,902	24,110	28,241	19,945	25,014
Mean temperature of water .....	18.1	18.8	18.0	18.0	32.1	37.4
Average steam-pressure—atmospheres....	3.5	3.18	3.02	3.18	2.84	2.87
Kilos. of water per square meter of heating surface .....	27.6	26.6	29.5	29.5	23.9	24.7
Coal per square meter of hearth .....	127.5	123.8	116.0	116.6	87.5	86.3
Consumption of coal.....	2548	2804	2782	3290	2450	2900
1 kilo. coal evaporates water, producing 600 units of heat.....	9.604	9.724	9.13	9.054	8.384	8.806
Ash, clinker, and dross.....	163	174	241	348	367	357
Theoretical fuel value of the coal—heat-units .....	7505	7364	7471	7504	—	7235
Fuel value taken up by the water—units	5762	5884	5478	5432	5030	5284
Loss through flue gases .....	1660	1310	1291	1333	—	1492
Loss through hearth-residues—units .....	146	162	375	482	408	279

Regnault and Reiset have shown that the breathing of animals in air containing 10 per cent. of oxygen is increased in rapidity; whilst air containing 4 to 5 per cent. of oxygen is incapable of sustaining life. According to Müller, breathing is retarded in air with 5 to 7.5 per cent. of oxygen; whilst air with 15 per cent. of oxygen does not affect the respiratory process. If the quantity of oxygen in the atmosphere be reduced to 4—7 per cent., and the exposure to such air continued for any length of time, a diminution in the oxidative processes in the human body takes place, which may be neutralised by an increase in the respiratory functions. The quantity of carbonic anhydride necessary to act on the animal organism is very considerable. Thus, Friedländer and Herter found that on breathing air diluted with 20 per cent. of carbonic anhydride, animals exhibited no toxic effects, but merely showed signs of their respiratory organs having been excited, and the work of the heart increased. The atmosphere of the natural hot baths of Oeynhausen, although containing several per cent. of carbonic anhydride, can be inhaled for 30 to 60 minutes without difficulty. Since, therefore, the changes in the normal constituents of the atmosphere are quantitatively insufficient to explain the ill-effects of the air in rooms, it has been thought that besides carbonic anhydride, other substances contained in small quantities in air are exhaled by the human body, which, being gradually re-inhaled, produce poisonous effects. The author has undertaken a series of investigations in this direction, as the conclusions at present arrived at have not been corroborated. He found that a small amount of organic matter is added to the air during respiration, as well as watery vapour. He, however, ascertained that under normal conditions man does not exhale volatile combustible products, at least not in appreciable quantity, and that when found in expired air their presence is due to the evolution of gases formed by defective digestion in the abdomen, especially in consequence of the introduction of improper food.

In conclusion, it is argued that the task of removing the expired gases from the surroundings of men by means of ventilation is of less importance than the question of limiting or preventing their formation. In order to breathe pure air, it is most essential to improve the diet as much as possible, and keep both body and dress free from dirt.

D. B.

**Bromine as a Disinfectant.** By A. FRANK (*Dingl. polyt. J.*, 249, 167).—The bromine is soaked up by infusorial earth, and is conveniently placed in a Brüner's pan of glass or porcelain, instead of lead, having a very deep depression in the cover.

The water sealing the joint of the lid becomes charged with bromine from the interior, whence the bromine gradually diffuses into the room. To accelerate the rate of diffusion, warm water may be poured into the depression in the centre of the cover.

Frank recommends petroleum to reduce the action of bromine on organic substances with which it may come into contact, or to quickly remove its odour.

J. T.

**The Salt Work of Giraud in France.** By G. LUNGE (*Dingl. polyt. J.*, 249, 517—523).—The salterns of Giraud belong to the great firm of Pechiney and Co., who own also the works of Salindres, where the manufacture of soda, chloride of lime, potassium chlorate, sodium chlorate, and aluminium is carried on. The company has the right of possession over an area of 20,000 hectares of water, which comprises the greater part of the lakes of Carmague, but only a small portion of these is at present worked, the actual evaporating surface embracing only 1,500 hectares. The junction with the sea consists in a narrow creek known as "Grau de la dent," leading to a branch of the Rhone, which is cut off from the land. At a distance of 3 kilos. from the inlet, a large steam pump is stationed, which raises the partly concentrated sea water to a height of 0·7 meter, and delivers it into a large primitive lagoon having an area of 250 hectares called "Étang de la Galère." The water then flows into the actual evaporating spaces (surfaces évaporantes, partènements, chauffoirs) arranged in groups round a reservoir of considerable size, called the "Cuvette," which occupies the lowest position in the series. The sea water which at the commencement has a density of 3·6° B. gradually increases in concentration, and at 16° B. deposits considerable quantities of calcium sulphate. By carefully regulating the supply of sea water it is possible to obtain a brine in the "cuvette," having a concentration of 25° B., so that 1 cubic meter of sea water is condensed to 102 litres. This process is usually commenced in the month of May, and is ended in about 120 days. From the "cuvette" the liquor passes through a channel, from whence it is pumped into raised salt beds (tables salentes), which are 140 meters in length and width, and 30 cm. in depth. The separation begins as soon as the brine reaches a density of 25·6° B., a layer of salt 1 mm. thick being obtained every day corresponding with the evaporation of a column of water 6 to 7 mm. in height. At the end of the evaporating process 1 hectare of salt bed yields a layer of salt 30 to 55 mm. in thickness, equivalent to 800 tons of salt.

At Giraud, three varieties of salt are produced, the first being obtained from a brine having a density of 25·6 to 27° B.; the second from the mother-liquors of the first, when they have reached a concentration of from 27° to 28·5° B.; and the third from the mother-liquors of the second after they have been concentrated to 31° B. The following analyses illustrate the composition of these varieties. I. Table salt; II. Salt for works; III. Salt for salting, &c.:—

	CaSO <sub>4</sub> .	MgSO <sub>4</sub> .	KCl.	MgCl <sub>2</sub> .	NaCl.	H <sub>2</sub> O.	Insoluble.
I.	1·115	0·221	—	0·100	97·100	1·400	0·050
II.	0·621	0·506	trace	0·377	94·212	4·201	0·030
III.	0·440	0·612	0·122	1·300	91·217	5·758	0·050

The final liquors when allowed to evaporate to a strength of 32·5° to 35° B. deposit the so-called "sels mixtes," a mixture of sodium chloride and magnesium sulphate. The residual mother-liquors are transferred to large cisterns, and deposit in the winter at a temperature of + 12° crystallised Epsom salt. The temperature should not

be less than  $12^{\circ}$ , otherwise carnallite crystallises out with the magnesium sulphate. The liquor remaining after the separation of the magnesium sulphate has a density of  $33^{\circ}$  B., and is worked up in the factory. 1 cubic meter of sea water yields only 16 liters of this final mother-liquor.

In conclusion, the author refers to some improvements made by Pechiney in dehydrating the vast quantities of hydrated sodium sulphate obtained by submitting the mixed solutions of sodium chloride and magnesium sulphate (sels mixtes) to artificial refrigeration by means of Carré's machine, when double decomposition takes place, crystallised sodium sulphate and solution of magnesium chloride being produced, which are then separated from each other by means of hydro-extractors. Pechiney adds 45 per cent. of "sels mixtes" to the hydrated sodium sulphate, and heats to  $80^{\circ}$ , when anhydrous sodium sulphate is obtained, which is then separated by machining. The whole process is performed in a short time, and its cost is very small. The filtrate is used for the production of more hydrated sulphate. With the view to separate potassium chloride in the form of carnallite from the mother-liquors which have deposited magnesium sulphate during the winter season, the solutions must be mixed together whilst hot, and in as concentrated a form as possible.

D. B.

**Commercial Sodium Nitrite.** By P. MACEWAN (*Pharm. J. Trans.* [3], 14, 121).—The author has examined several samples of this salt, and finds that they contain widely different proportions of nitrite. He points out that by fusing the sodium nitrate with lead or copper, instead of carbon, a much purer product can be obtained. He also suggests that old stock of sodium nitrite (a sample analysed contained only 0.028 per cent.  $\text{NaNO}_2$ ) should be looked over, and that the fused nitrite of soda of the 1864 Pharmacopœia—a sample analysed contained only 9.6 per cent.  $\text{NaNO}_2$ —should not be dispensed.

D. A. L.

**Improvements in Metallurgy.** (*Dingl. polyt. J.*, 250, 79—88, and 123—133.)—Referring to the reduction of agglomerated mixtures of ores and flux in zinc ovens, Binon suggests that the mixings should be introduced into the oven in a strongly compressed state. Hitherto it has been supposed that by adding the mixings in a finely divided state the carbonic oxide would penetrate more readily and deeply into the mass, and thus facilitate the reduction process. This Binon disproves. In a pressed form it is possible to fill the distillation tubes with 50 per cent. more charge, a saving of 10—15 per cent. being simultaneously effected in the amount of reducing agent required.

Egleston states that the presence of tellurium in copper is injurious. Samples of black copper from Colorado ores evolved fumes of tellurous anhydride when refined. The following is the composition of the matter of two samples of the black copper and of the refined copper:—

	Matte.	Black copper.		Refined copper.
Cu .....	55·02	97·120	98·090	99·705
Au .....	0·06	—	—	—
Ag .....	0·40	0·132	0·128	0·135
Pb .....	17·87	0·777	0·757	—
Zn and Ni..	2·22	0·070	0·100	0·024
Fe .....	4·18	0·130	0·080	0·031
S.....	20·02	0·236	—	traces
Te .....	0·12	0·093	0·097	0·083
As .....	—	0·006	—	0·091
Slag, &c. ..	—	1·270	0·192	—
	99·89	99·834	99·444	100·069

The refined copper had all the appearance of being good copper, but on rolling it into plates 30 mm. in thickness, very fine cracks showed themselves, which penetrated the plate on each side. At a thickness of 8 mm. it began to fall to pieces. When cold the metal was tough and malleable.

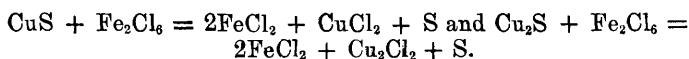
In copper smelting, the treatment of the coarse metal in the Bessemer converter has been practised since 1866. Manhes has recently worked up the coarse metal at Eguilles and Vedènes in this manner. In the commencement a converter with a charge of 200 kilos. was used. The bottom of the converter communicated with a blast chamber and a number of vertical tuyeres. It was, however, found more expedient to employ horizontal tuyeres, and to introduce the air into the metal bath some distance above the bottom of the converter, as the vertical tuyeres soon became blocked, owing to the fact that at the end of the operation the heat did not suffice to keep the metal bath and the ferruginous slag in a fluid condition. The apparatus worked satisfactorily, and the copper produced did not contain more than 1·5 per cent. of foreign ingredients. In the case of poorer ores the process was divided into two operations, in the first the coarse metal was blown until it contained 60 per cent. of copper, the slag was then removed and the operation completed in a second converter. Manhes has refined coarse metal of various degrees of purity, also ores containing arsenic, antimony, lead, zinc, &c. The foreign constituents are volatilised or scorified, and it is recommended to add ferromanganese to the impure copper, in order to render the slag more fluid. The process is of importance where fuel is expensive and cheap water power at disposal.

Johnsson proposes to fuse sulphuretted copper ores in a Pils-Mansfeld furnace provided with 6 or 8 tuyeres. The resulting product, containing about 35 per cent. copper and 26 per cent. sulphur, is then worked up into black copper in a Siemens furnace.

The treatment of the Riotinto cupriferous ores is described in detail in the *Allgemeine Metall. Zeit.*, 1883, 1. The exported ores contain 3—3·5 per cent. of copper, and are used in England and Germany for the manufacture of sulphuric acid. The burnt residues are worked up for copper and silver in the usual manner. After referring to the

roasting of the ores rich in copper, as conducted at Riotinto, the extraction of copper and its precipitation by iron is discussed. It is stated that owing to the fact that 1 ton of refined copper requires 2 tons of pig-iron, this process is being gradually abandoned, and the precipitation of the copper effected by means of hydrogen sulphide. The final liquors, which should be free from hydrogen sulphide, can be used for lixiviating purposes, as they contain free acid.

The roasting of the ores has been abandoned at two experimental stations of the Riotinto works. In its place the Dötsch process is used, which resembles the method introduced by Kopp and Chalandre. According to Cumenge and Wimmer, this method of extracting copper is applicable to pyrites containing on an average 2.68 per cent. of copper. The metal is present as  $\text{CuS}$  and  $\text{Cu}_2\text{S}$ . On treatment with ferric chloride the ores are decomposed according to the equations—



The practical utility of these reactions consists in the circumstance that the ferric chloride in solution attacks the cupriforous pyrites or the copper sulphides, whilst the iron pyrites remains unaltered. Instead of ferric chloride, a solution of ferric sulphate and salt may be used, which suffers decomposition into sodium sulphate and ferric chloride. This solution is allowed to percolate slowly through the ores piled up in heaps. 1 cubic meter of the filtered liquor contains 5—6 kilos. copper, mainly in the form of cuprous chloride, hence the consumption of iron for precipitation is considerably reduced. The residual solution of ferrous chloride is converted into the ferric salt, and used for a further operation. The conversion is effected by means of chlorine obtained by heating a mixture of rock-salt and ferrous or ferric sulphate in a reverberatory furnace provided with three doors, the combustion-products being supplied with a current of air introduced into the furnace through the fire bridge.

It is stated that on roasting ores containing lead, silver, copper, or nickel, and antimony or arsenic with sodium chloride, according to the process for roasting antimonial ores introduced by Lyte, fumes of the chlorides of silver and lead are given off, besides antimony and other volatile chlorides. To prevent this loss, the roasted or non-roasted metallic sulphides are subjected to the action of hydrochloric acid at  $250\text{--}400^\circ$  in reverberatory or muffle furnaces. The less volatile chlorides of silver and lead remain in the residue, whilst the chloride of antimony is volatilised, its vapour being condensed in hydrochloric acid. The chlorides of silver and lead are extracted by means of a hot solution of salt; on cooling, lead chloride separates in a crystalline form. The separation of the silver and the remainder of the lead from the decanted solution is effected by means of zinc.

Helmhacker (*Bergund. Hüttenm. Zeit.*, 1883, 191) enters into a long discussion on the processes for recovering and refining antimony. According to Föhr, the Boëtius furnace is now largely used in Upper Silesian zinc works, and is preferred to the Siemens furnace.

D. B.

**Metallic Alloys.** (*Dingl. polyt. J.*, **250**, 31—36.)—For the preparation of alloys of chromium with iron, and of tungsten with iron, Guétat and Chavanne recommend to mix the soluble salts of the two metals in the required proportions, and precipitate them by double decomposition as chromate or tungstate of iron. The precipitates are then dried, roasted, mixed with carbon, and heated to whiteness in well-luted graphite crucibles. For the preparation of cupric phosphide, cupric chloride is decomposed with calcium phosphate, and the resulting cupric phosphate reduced in graphite crucibles.

According to Dick, the hardness and toughness of alloys of copper and tin, and copper and zinc, is increased by the addition of small quantities of iron.

Seyboth proposes to clean metals and metallic alloys by means of an aqueous solution of potassium or sodium carbonate and calcium phosphate, mixed with pulverised charcoal to a stiff paste, which is then added to the fused metal or metallic alloy. For cylinders used in calico printing, Hauvell recommends an alloy of the following composition:—Cu = 86, Sn = 14, and Zn = 2. Rendel analysed English cylinder metal, and found it to contain Cu = 5·6, Zn = 78·3, and Sn = 15·8. Although these proportions yield a hard fine-grained alloy, it is thought that the dye-stuffs employed in printing would readily attack the same. Analyses of the doctors used in printing gave the following numbers:—

	Cu.	Zn.	Sn.
Yellow French doctor according to Salvétat ..	78·75	12·50	8·75
Yellow English doctor according to Berthier ...	80·50	10·50	8·00
Yellow German doctor according to Elsner ....	85·80	9·80	4·90

From a series of trials it is concluded that besides the red cuprous oxide, alloys containing 25—30 per cent. zinc, and 75—70 per cent. copper, are most suited for printing purposes. The presence of lead is condemned.

D. B.

**Bessemer Process.** (*Dingl. polyt. J.*, **249**, 264—269.)—As an appendix to a former paper, Finkener shows that in the basic process silicon and manganese first diminishes, then the carbon, and lastly, the phosphorus and manganese, if the latter has not already disappeared with the silicon. Experiments show that the carbon is removed as carbonic oxide essentially, with but very little carbonic anhydride, but the relative amount of the two may vary with the temperature and quality of the iron, the carbonic anhydride disappearing only when the iron is rich in carbon. The phosphorus is oxidised to phosphoric anhydride simultaneously with so much iron that a bibasic ferrous phosphate is formed; a compound with less iron cannot separate out from the fluid iron, as the latter decomposes it. So long as silicon is present, carbonic oxide is reduced as fast as produced, silicate and carbide being produced. Ferro-silicon is so powerful a reducing agent that under its action normal ferrous silicate yields part of its iron in the metallic state. The more easily reduced phosphate is decomposed, so that no phosphorus is removed so long as any silicon remains. As the silicon protects phosphorus, so does manganese



protect iron. After removal of the silicon, carbonic oxide is evolved containing some little carbonic anhydride; the latter increases slightly in amount as the carbon in the iron diminishes. Manganous or ferrous phosphate is formed, but only to a slight extent, the greater portion being reduced again by the iron carbide present. This reduction can only be ascribed to the mixed carbonic oxide and anhydride, on the supposition that the reducing power of the gaseous mixture increases more rapidly with a rise in temperature than does that of the carbide.

Metallic iron picked out of the slag is found to contain little phosphorus, but if carbonic oxide acted reducingly on the phosphate in the slag this iron might be expected to be richer in phosphorus. If iron carbide is the reducing agent, the phosphide produced combines with iron. When carbon has been removed, the separation of ferrous phosphate proceeds, since this compound can exist along with iron. Iron sulphide is undecomposed after the dephosphorisation; it can exist during the formation of iron oxide. A small amount of sulphur remains almost unchanged; a larger amount of sulphur is reduced, owing to the action of the slag on the iron. After the addition of spiegel, the amount of phosphorus increases, some of the phosphate in the slag being reduced, probably, as mentioned above, by the iron carbide now present again. The author gives details of experiments showing the action of silica, phosphoric acid, ferrous phosphate and pyrophosphate, sulphurous anhydride, and calcium sulphite, on metallic iron, the substances being heated up to whiteness in a porcelain tube.

J. E. Stead gives analyses of gannister from Sheffield used for Bessemer vessel linings, also analysis of basic lining as follows:—

CaO.	MgO.	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> .
49·91	30·72	4·50	3·46	11·41 = 100·00

This is mixed with tar and rammed in the vessels, or previously moulded into blocks. The pig-iron now used for the acid process may contain as much as 0·15 per cent. sulphur, whilst formerly 0·05 was the maximum limit; this is due to the richer spiegel now obtainable, so that more manganese can now be added to counteract the effect of the sulphur. The following figures show the changes taking place during an ordinary blow:—

	Beginning of the blow.	After 5 min.	10 min.	15 min.	20 min.	25 min.
C.....	3·5	3·6	3·3	3·25	2·0	trace
Si ....	2·25	1·0	0·5	0·2	0·1	trace
Mn ....	1·00	0·35	0·2	trace	—	—

During a *hot* blow the carbon burns more quickly, thus:—

C.....	3·5	3·6	3·3	2·5	1·0	trace
Si ....	3·0	1·75	0·25	0·9	0·7	0·5
Mn ....	0·75	0·25	trace	—	—	—

The flame does not drop so readily during a hot blow, and the

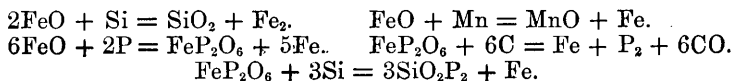
blast is continued until brown fumes of burning iron appear. With increasing temperature consequently the affinity of oxygen and carbon increases, a circumstance of importance in the production of compact castings by the addition of silicon, since the silicon ceases to act as soon as the affinity of oxygen to carbon exceeds that of oxygen to silicon. Pig-iron suitable for the basic process has the following composition :—

C.	Mn.	Si.	S.	P.
3.35	0.60	1.30	0.15	1.75
to	to	to	to	to
3.50	1.00	1.00	0.12	2.75

After the addition of 15—17 per cent. of lime, the following changes take place during a blow :—

	Beginning of the blow.	After 5 min.	10 min.	15 min.	18 min.
C.....	3.50	3.55	2.35	0.07	trace
Si ....	1.15	0.50	0.09	trace	—
Mn ....	0.71	0.56	0.27	0.12	trace
P.....	1.57	1.60	1.43	1.22	0.08
S.....	0.16	0.14	0.13	0.12	0.10

The highly basic ferruginous slag formed is again decomposed, and the more readily the more intimately it is mixed with the iron. The following formulæ show these various reactions :—



So long, therefore, as silicon and carbon are present, and a thick bath of iron exists over the tuyeres, practically no phosphorus is removed. On the contrary, with a shallow bath of iron and a powerful blast so that the slag is kept well on the surface, phosphorus can be removed before the whole of the carbon has gone, as Thomas and Gilchrist found in their early experiments. With an acid lining, phosphorus is not removed, since calcium and iron phosphates are converted into silicates by silica, with separation of phosphoric acid, which latter then gives phosphorus and ferrous oxide under the action of iron. Analyses of the slags produced are given by the author, and also of the resulting steel. J. T.

**Modern Processes for the Manufacture of Iron and Steel and the Properties and Methods of Testing these Materials.** By F. KUPELWIESER (*Dingl. polyt. J.*, 250, 37—46).—The author states that the manufacture of iron and steel embraces processes belonging to the category of indirect processes, as the iron ores are smelted in order to obtain pig-iron therefrom, which is then subjected to oxidation processes. These have for their object the separation as far as possible of foreign substances which accompany the iron, and the conversion of the metal into soft iron or steel, eliminating at the

same time more or less carbon. The efficiency of the separation of the impurities depends on the oxidation process employed; as to whether the end product of the oxidation process is obtained as spongy blooms or in a perfectly fluid condition depends on the final temperature. By conducting the refining in hearth and reverberatory furnaces, loose spongy iron masses are obtained, from which it is difficult to remove all the slag. In order to obtain a fluid product, the puddled iron is subjected to a final operation of reheating to a welding temperature. The great drawback to this process is its cost, and the difficulty of obtaining a homogeneous product. It has therefore been gradually abandoned.

Chief among the modern refining processes ranks the Bessemer process, which has been brought to further perfection by the improvements introduced by Thomas and Gilchrist. The Siemens-Martin process differs from the final operation of remelting the metal in crucibles by the iron being heated on the open hearth of a regenerative furnace, otherwise it bears great resemblance to the old process of reheating.

Referring to the properties of iron and steel, it is mentioned that they are influenced by the quantity and quality of the foreign substances present, also by the homogeneity of the material and the mechanical treatment to which the metal is subjected. The conditions most suited for the production of the best kinds of iron are the entire absence of foreign constituents except carbon, and the presence of the latter in quantities sufficient merely to impart to the metal its requisite degree of hardness, firmness, elasticity, &c. It is difficult but not impossible to obtain such a product on a large scale.

The author discusses the changes in the properties of iron caused by the presence of foreign ingredients, such as carbon, silicon, manganese, sulphur, and phosphorus; he also refers to the question as to the production of sound castings free from porous and blistered places. The paper, which is of considerable length, examines minutely the probable causes and effects of the differences in the mechanical treatment, temperature used, and uniformity of the raw material employed; and concludes with some remarks in connection with the testing of rails.

D. B.

**Notes on the Dephosphorisation of Iron.** By G. HILGENSTOCK (*Dingl. polyt. J.*, **250**, 330).—The slag obtained in the basic process worked at Hörde frequently exhibits a crystalline appearance. Selected specimens of crystals gave by analysis 61.1 per cent. lime and 38.14 per cent. phosphoric acid, corresponding with the formula  $\text{Ca}_4\text{P}_2\text{O}_6$ .

According to Carnot and Richard, basic slag from Joeuf contained blue translucent crystals of the following composition:—

$\text{P}_2\text{O}_5$ .	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{FeO}$ .	$\text{MnO}$ .
29.65	12.42	2.76	53.20	traces	1.80	traces
						D. B.

**Action of Organic Acids on Nickel-plated Iron Vessels.** By K. BIRNBAUM (*Dingl. polyt. J.*, **249**, 515—517).—Culinary vessels

made of nickel-plated iron have recently been brought into commerce, and from their pleasing appearance will probably be rapidly introduced into kitchens. It is not unlikely that these vessels will be used without due regard to the various operations in connection with the preparation of food, as in recommending them reference is made to a statement by Schulz that 2 litres of milk, when kept in a nickel pan for eight days, dissolved only 0.022 gram of metal, and that a dog received during 21 days a total of 10.5 grams of nickelous acetate without exhibiting any marked symptoms. The author has made a series of experiments, and found that by working with a much smaller quantity of liquid than that employed by Schulz, considerably more than 0.022 gram of metal was dissolved, so that the thin coating of nickel would soon disappear. Referring to the physiological experiments on the toxic action of nickel and its salts, it is doubtful whether human beings will not be affected in a different manner; moreover, it is not shown whether the nickel compounds pass rapidly through the system or remain in the same, in the latter case, the period of observation of three weeks was scarcely sufficient to determine to what extent nickel is poisonous. Until this has been definitely decided, nickel-plated vessels should be used with great caution, and their use wholly abandoned for the preparation of hot foods.

D. B.

**Polished Brass.** By MEIDINGER (*Dingl. polyt. J.*, 250, 330).—About 10 years ago large slabs, plates, signs with ornaments, heads, &c., pressed out of thin sheets of brass in slight relief, were brought into the market from Antwerp, representing imitations of ancient brasses. They were called *cuivre repoussé*, and were used for decorating walls. About the same time small artistic objects, such as candlesticks, inkstands, ashtrays, &c., cast in brass, were introduced into commerce as coming from Paris under the name of *cuivre poli*. Their manufacture was subsequently taken up in Berlin, where the best articles were prepared. In order to obtain a fine polished surface, the castings were turned in a lathe, into which wire brushes, emery discs, and polishing cloths are fixed.

D. B.

**Contribution to a Knowledge of Mineral Fuel.** By BOUSSINGAULT (*Dingl. polyt. J.*, 250, 331).—The author has examined bitumen from the hot springs of Ho-Tsing in the province of Szu-Tchaun, China. It is fluid at the ordinary temperature, but deposits naphthalene (?) on cooling. Composition:—

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.
Fluid ....	86.82	13.16	—	0.02
Solid ....	82.85	13.09	4.06	—

Asphalte from Egypt (I) and mineral pitch (Jew's pitch) from the Dead Sea (II), gave by analysis:—

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.
I .....	85.29	8.24	6.22	0.25
II .....	77.84	8.93	11.53	1.70

Fossil resin resembling amber, from the alluvions of New Granada, found in one piece weighing 12 kilos. at the gold washing works of Giron, near Bucaramanga (I), and fossil resin from the deltas of Antioquia (II), gave :—

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.
I .....	82.70	10.80	6.50	—
II .....	71.89	6.51	21.57	0.03

Coal from Canoas, on the plateau of Bogota, Cordilleras (I), and coal from the province of Antioquia (II), had the following composition :—

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.
I .....	80.96	5.13	12.50	1.41
II .....	87.05	5.00	6.56	1.39

Coal resembling wood-charcoal, hence called "Fusain," from the mines of Blanzi (I) and Montrambert, Loire (II), gave by analysis—

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.
I .....	87.81	3.88	7.67	0.64
II .....	93.05	3.35	3.43	0.17

Anthracite from Chili (I) and Muso, New Granda (II), gave—

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.
I .....	92.25	2.27	4.94	0.54
II .....	94.83	1.27	3.16	0.74

Graphite from Karsoh contained—

Carbon.	Hydrogen.	Oxygen.	Nitrogen.
97.87	0.37	1.70	0.06

On treatment with dry chlorine gas at a red-heat, pure carbon was obtained.

D. B.

**Geological and Chemical Investigation of Bentheim Asphalte with reference to Analogous Occurrences in Italy.** By STRIPPELMANN and ENGLER (*Dingl. polyt. J.*, **250**, 216—227, 265—271, and 316—321).—In the first part of the paper, Strippelmann speaks of the occurrence of asphalte at Bentheim, and of similar asphaltic deposits at Paterno, Castro, Colla San Magna, and other places. He then enters into a minute discussion on the formation of these bitumens. His conclusions confirm the views held by Mendelejeff as to the formation of bitumen by inorganic means. Bitumen is frequently met with at places where, from a geological point of view, its occurrence can be explained only by duly recognising the theory as to the direct influence of volcanic forces on the formation of fissures, and by assuming that the bitumen accumulated within the fissures is formed in the same manner as that contained in lavatic geodes, and separated from prehistorical tufaceous deposits, but by inorganic means.

In regard to the practical utility of the Bentheim asphalte, it is stated that it is of high value for the purpose of gas-making and for the preparation of burning oil, paraffin, lubricating oil, and coke. According to Engler the asphalte has a sp. gr. of 1.092. It is insoluble in alcohol, ether, carbon bisulphide, oil of turpentine, and similar solvents, and melts when heated strongly. It contains—

	I.	II.
Carbon .....	89.46	89.33
Hydrogen .....	9.55	9.88
Residue (ash) .....	1.09	1.14

The following products are obtained on fractional distillation :—

1. Distilled in glass retorts without steam—

	I.	II.
Tar.....	36.8	38
Coke .....	48.9	48
Loss (gas and water)	14.3	14

The tar has a sp. gr. of 0.834, and forms a thick semi-liquid mass of dark colour, boiling at 80° and yielding the following fractions when subjected to distillation :—

At 150°. 10.3 per cent. oil. Sp. gr. 0.743.  
 150—310°. 43.3 per cent. burning oil. Sp. gr. 0.806.  
 Residue, 46.4 per cent.

2. Distilled in glass retorts by the aid of steam :—

	I.	II.
Tar.....	41.4	41.8
Coke .....	43.5	45.0
Loss (gas and water)	15.6	13.2

The tar has a sp. gr. of 0.853, and yields by fractional distillation :—

At 150°. 7.1 per cent. of oil. Sp. gr. 0.743.  
 150—310°. 34.4 per cent. of burning oil. Sp. gr. 0.805.  
 Residue, 58.4 per cent.

3. Distilled in stills or retorts on a large scale :—

(a.) *Cast-iron Stills.*

	I.	II.
Tar.....	33.0	34.5
Coke .....	47.0	45.0
Loss (water and gas)	20.0	20.5
Sp. gr. of the tar = 0.0838.		

(b.) *Cast-iron Horizontal Retorts.*

Tar.....	28.66
Coke .....	46.09
Loss (gas and water) .....	25.25
Sp. gr. of the tar = 0.830.	

The tar obtained by the distillation of the asphalt on a large scale was free from phenol and creosotic compounds. On treatment with 4 per cent. sulphuric acid (containing 95 per cent.  $\text{H}_2\text{SO}_4$ ) at  $60^\circ$ , 94 per cent. of refined tar was obtained, this when rectified over 0.4 per cent. caustic soda in cast-iron stills yielded the following products:—

*Light Oils 25.5 per cent.*

Oil .....	2.0	2.4	2.4	2.4	2.4	2.4	11.5
Sp. gr. ....	0.776	0.785	0.786	0.789	0.791	0.795	0.805

*Medium Oils 21.8 per cent.*

Oil .....	10.8	11.0
Sp. gr. ....	0.822	0.834

Oil..	44.8	2.4	3.2	2.3
Paraffin mass		Paraffin grease	Coke	Loss of gases

making 100 in all.

The paraffin was separated from the oil by cooling, filtering, and pressing. Obtained:—

9.91 per cent. crude paraffin, melting point  $51^\circ$   
90.09 per cent. oil, sp. gr. 0.864.

Hence, by subjecting Bentheim asphalt to distillation on a large scale, the following products are obtained:—

Burning oils .....	12.72
Gas and lubricating oils .....	9.78
Paraffin .....	1.50
Paraffin grease .....	0.65
Coke from retorts .....	46.09
Coke from tar .....	0.86
Pitch .....	1.52
Loss (gas and water).....	26.88
	<hr/>
	100.00

A series of carbonising trials, made with Bentheim asphalt, showed that the yield of gas obtained largely exceeded that of other kinds of gas-coal.

Engler has investigated Italian petroleum from Terra di Lavoro. The crude oil forms a dark brownish-black thick fluid, having an unpleasant smell. It has a sp. gr. of 0.970 at  $21^\circ$ , and gives by analysis:—

	I.	II.	III.	IV.
Carbon.....	83.72	83.52	—	—
Hydrogen ..	10.71	10.88	—	—
Sulphur ....	—	—	1.08	1.30

Besides hydrocarbons, oxygenated resinous substances are present

in large quantities, also sulphur compounds. Paraffin could not be detected, although by subjecting the crude oil to fractional distillation the higher boiling portions deposited small quantities of paraffin on cooling. It is doubtful, however, whether it has not been formed by distillation. Cumene, which has been detected in most kinds of petroleum (Pennsylvania, Galicia, Baku, Alsace), was found also in this variety. Phenols or creosote are absent. Owing to the high boiling point and high specific gravity, this oil cannot be used for burning purposes; it is, however, specially adapted for the manufacture of lubricating oils. The subjoined table gives the results of experiments on the quantity and properties of the gas obtainable from Italian petroleum :—

Investigator.	Sp. gr. of the petroleum.	Quantity of petroleum used in the trial.	Duration of the distillation in hours.	Gas for 1 kilo. of petroleum.	Petroleum required for the production of 24 cubic meters of gas = 100 candles per hour.
		kilos.		cub. meters.	kilos.
P. Jacques, Turin ....	0·975	10·50	2·00	0·439	9·11
	0·975	16·80	2·00	0·487	8·21
L. Ferrario, Rome....	0·975	11·00	1·55	0·431	9·27
	0·975	14·90	2·00	0·426	9·39
F. Scheuer, Lugano ..	0·975	17·70	1·33	0·325	12·31
	0·925	15·90	1·32	0·384	10·40
Sulzer Bros., Winterthur .....	0·975	16·80	1·59	0·454	8·81
	0·925	13·20	2·00	0·560	7·13
Anonymous Society for water and gas installation, Vienna .....	0·975	30·00	2·00	0·456	8·77
	0·925	30·70	1·42	0·457	8·74
H. Hirzel, Leipzig....	0·975	14·70	1·39	0·421	9·50
	0·925	16·00	1·30	0·264	15·13

The oils of 0·925 sp. gr. are rectified, the remainder crude petroleum.

In conclusion, it is stated that although the boiling points of the various fractions obtained by the distillation of Italian petroleum and Bentheim asphalt correspond with one another, there is a marked difference in their respective specific gravities. For example, the fraction boiling below 290° has a sp. gr. of 0·882 in the case of the Italian oil, whilst the density of the corresponding fraction from the oils obtained from Bentheim asphalt, is below 0·880. Engler is of opinion that such wide differences in the density of the same boiling fractions of various mineral oils, have not been observed hitherto; this circumstance proves how variable the internal constitution of these hydrocarbons must be, although they may belong to the ethane or ethylene series.

D. B.

**New Bye-product from Coal Distillation.** By G. E. DAVIS (*Chem. News*, 48, 229).—With regard to the distillation of coal, &c.



(comp. this vol., 224), attention is drawn in the present paper to the use of gas for heating and cooking purposes, and as it is generally acknowledged that for such purposes a luminous and smoky flame is not desirable, therefore, before being applied to this use, the gas may with advantage be deprived of illuminants. Now, in the author's opinion, all the published analyses, &c., of coal-gas, are misleading, valueless, and inaccurate, inasmuch as he finds, from experiments, that the chief illuminants of coal-gas are not ethylene, diethyl, &c., but the vapours of easily condensable hydrocarbons, beginning to boil at 18°, and containing many hydrocarbons, including naphthalene. These illuminants are easily absorbed by olive, rape, or even hydrocarbon oils; and the absorption can be made so complete that the gas after treatment burns with a flame of exceedingly feeble luminosity. Five gallons of condensed hydrocarbons of great technical value can be obtained from the gas yielded by one ton of coal; the author proposes to call them "crude benzol." The quality of the "crude benzol" depends greatly on the temperature, both within and outside the retorts, and therefore if their recovery is contemplated, heating operations must be conducted with greater care than is necessary in ordinary gas making. The presence of paraffins in the "crude benzol" is proved by the short yield of aniline obtained from them.

D. A. L.

**Artichokes a Source of Spirit.** (*Bied. Centr.*, 1883, 856.)—The spirit made from artichokes is somewhat cheaper than that from potatoes, and when potato disease is prevalent it is advantageous to employ this plant.

E. W. P.

**Evaporation of Alcohol from Wooden Vats.** By A. SCHROBE (*Bied. Centr.*, 1883, 854).—During the first year the loss was 0·73 per cent. monthly, during the second year 0·42 per cent. monthly, in the third 0·42, in the fourth 0·31, in the fifth 0·31, and in the sixth, seventh, and eighth years 0·21 per cent. monthly.

E. W. P.

**Presence of Arsenic in Wines Free from Artificial Colouring-matter.** By A. BARTHÉLEMY (*Compt. rend.*, 97, 752).—Some wine sold in the department of Midi was found to contain a relatively considerable quantity of arsenic. This wine had been kept in old barrels, whilst the same wine stored in new barrels was free from arsenic. The arsenic was derived from sulphuric acid with which the old barrels had been repeatedly washed, and which, as sold in the neighbourhood of Toulouse, contains a large proportion of arsenic.

C. H. B.

**Steeping of Barley.** By F. ULLIK (*Bied. Centr.*, 1883, 639—641).—The author continues the experiments already noted (*Abstr.*, 1882, 645 and 761), on this occasion to ascertain the effect of different quantities of water and frequent changes; the water had nearly the same composition as that previously used. He found that when the same quantity was used frequent changing had no appreciable influence, but that the employment of larger quantities extracts more matter from the barley, and more lime enters the grain. The potash dissolved is not greatly different, but soda, lime, magnesia, and

phosphoric acid increase, as do organic matters, carbohydrates and nitrogen particularly. The use of water containing a small percentage of sodium chloride withdraws lime, and causes soda to enter into the grain. Further experiments convince the author that the condition of the barley itself has more effect on the substances withdrawn during steeping than the quantity or quality of the water, and that greater quantities of extract are to be had from old than from fresh barley. As the nitrogenous substances possess particular interest, the author made a steep of 600 grams barley, and found a total of 0.133 gram nitrogen, of which 0.112 gram remained in the residue from the phosphotungstic filtration. No peptones were traceable, and the bulk of nitrogenous matter was derived from amides. The author has begun experiments which show that steeping causes changes to occur which are intimately connected with the life and growth of the grain.

J. F.

**Employment of Maize in Brewing.** By J. F. GENT (*Bied. Centr.*, 1883, 853).—According to this patent, the corn is coarsely crushed between rollers and freed from husk and embryo, and then softened by steam, and finally pressed and dried between hot rollers. To brew from this, 65 parts are added to 35 parts of barley malt.

E. W. P.

**Pasteurising Beer.** By M. SCHWARZ (*Bied. Centr.*, 1883, 560).—According to Behrend, yeast cells are not killed by warming; the author, on the contrary, finds that at 55° all the cells are killed. Yeast killed at 55° placed in a food solution with addition of fresh malt-extract, did not show a single living cell after 40 hours at a temperature of 6—7°. Every single bottle of beer should be heated uniformly for a considerable time to the necessary temperature, say 2—3° over 55°. Badly pasteurised beer remains clear when kept cool, but the warmth of a room turns it turbid from formation of yeast, bacteria, fungi, albuminate, and some hop resin. The turbidity of well-pasteurised beer the author finds to be due to a separation of gluten; by heating such beer to 50° it will again become clear, and remain so for a long time.

J. T.

**Behaviour of Tannin in Hops towards the Albuminoids in Malt.** By MORITZ and LEE (*Bied. Centr.*, 1883, 854).—The tannin in hops precipitates as much again of the albuminoids in malt as simple boiling does; but there is a sufficiency of these compounds in the malt to feed the hops after all the tannin has been precipitated.

E. W. P.

**Separation of Sugar from Molasses or Syrup by Strontia or Lime at Low Temperatures.** By C. SCHEIBLER and others (*Bied. Centr.*, 1883, 637—639).—The author has taken out another patent relating to the strontia process, which is thus described. On boiling a mixture of sugar and strontia solution, the sparingly soluble di-strontium saccharate is precipitated; this does not occur in the cold, but either pure strontium hydroxide or monostrontium saccharate crystallises,  $C_{12}H_{22}O_{11}SrO + 5H_2O$ , and the latter is sure to happen provided a certain quantity of the compound obtained from a previous operation is stirred into the mixture of molasses and strontia. The

proportion yielding the best results is obtained by adding so much  $\text{Sr}(\text{HO})_2 + 8\text{H}_2\text{O}$  to the molasses as the latter contains sugar, the strontium hydroxide being previously dissolved in three times its weight of boiling water. The mixture remains clear while just under the temperature of boiling water, but on cooling, the monosaccharate separates in warty masses, which are dried by filter-presses or other means. The saccharate so obtained contains two-thirds or three-fourths of the whole sugar, and the remainder can be recovered as di-saccharate. The monosaccharate yields strontium carbonate and sugar when treated with carbonic anhydride. Another way of obtaining sugar from molasses in the cold is described by Walters, by the addition of sharply burnt lime, which first forms a soluble saccharate, but after a time becomes an insoluble compound—tetra-calcium saccharate. Much of the success of this process depends on the manner of burning the lime employed. Lippman says that if powdered calcium hydroxide be added to a solution already saturated with lime, at a moderate temperature, the sugar is precipitated in the cold as a tribasic lime salt with an excess of uncombined lime.

J. F.

**Manufacture of Maize-starch as a New Branch of Agricultural Industry.** By L. v. WAGNER (*Dingl. polyt. J.*, 250, 173—182).—This paper discusses in detail the manufacture of maize-starch, and the recovery of the bye-products (proteïds) for feeding purposes. The process recently introduced by Gillitzer has the advantage that in the preparation of starch from maize the proteïds are recovered in an unaltered condition, the yield of starch and of proteïds recovered being almost theoretical. The starch is of the best quality. 100 parts of maize produce 52—60 parts starch, 8—15 parts proteïds (maize fibrin and gluten), and 12—18 parts husks, &c. The author shows that the cultivation of maize in conjunction with the manufacture of maize-starch is more remunerative than the cultivation of potatoes. The recovery of the bye-products pays for working costs, so that the difference in the price at which the maize is bought and that at which the resulting maize-starch is sold is profit.

D. B.

**Researches by Witz on the Oxidation of Cellulose.** By H. SCHMID (*Dingl. polyt. J.*, 250, 271—280).—The methods for animalising vegetable tissues with a view to render them better able to receive colours in dyeing are based on the following reactions:—(1) nitration, (2) mercuration, the result of the action of alkalis, and (3) hydration of the cellulose, caused by the action of acids.

Witz has introduced a new process, in which any substance capable of producing oxidation may be employed. By the action of oxidising agents in acid or neutral solutions, textile fabrics are so altered as to enable them to more readily receive dye-stuffs. The author discusses the investigations of Witz more minutely. He considers that Witz's reaction depends on the conversion of cellulose—a carbohydrate constituted like an alcohol—into a compound having acid properties, so that its power to attract basic dye-stuffs is analogous to the affinity which characterises benzoic acid, tannin, and other aromatic acids.

Its action would in point of fact consist in the precipitation of insoluble compounds of the complex amines of the rosaniline-group and similar colouring matters. The resulting lakes do not, however, adhere to the fibre as firmly as the corresponding tannin colours. As oxidising agents, Witz has employed the hypochlorites, also hypochlorous acid disengaged from the hypochlorites, chromates, hydrogen peroxide, ozone, and atmospheric oxygen. The goods may, moreover, be simply exposed to light. D. B.

**Analysis of Malt-extract.** By J. F. C. JUNGK (*Pharm. J. Trans.* [3], 14, 104—108).—An extract of malt that is soluble in water, has a pleasant taste, and remains unfermented for a long time, is usually considered to be good, but as many worthless preparations have these characteristics their value cannot be ascertained from these alone. In the author's opinion, it should in addition be light in colour, contain but little free acid, and only a limited quantity of water; all the soluble constituents of the malt should be present, diastase being the most important, and the albuminoids should be in an easily digestible form. The presence of a large proportion of phosphates or other ash constituents is no criterion of a good extract. The author's analytical examinations are based on these considerations. The *solid matter and water* are best determined by means of a maltometer, or by taking the sp. gr. at 17.5° of a solution of the extract in an equal weight of water, and referring to a table given in the paper. A good extract should not contain less than 50 per cent. of extracted matter, as in dilute extracts, some beers, for example, diastase cannot exist, and the preparations are often treated with salicylic acid in order to delay the decomposition of the dextrin; this may be detected by agitating the extract with ether, evaporating the ethereal extract, and testing for the salicylic acid with ferric chloride. For the *determination of free acid*, the author employs a solution of soda containing 5 grams of sodium hydroxide to a litre of water, and very sensitive litmus-papers for the indicator. 10 grams of a good extract ought not to require more than 6 or 7 c.c. of the soda solution; if it requires more than 10 c.c., that is more than 0.5 mm. of soda for 100 c.c. of extract, it will not retain its diastatic power for long. The *determination of diastase* is conducted in the following manner. Several clear and uniform 2-oz. vials are charged with 2 ozs. of distilled water and 2 drops of iodine solution containing 2 grams of iodine and 4 grams of potassium iodide dissolved in 250 c.c. of water. 10 grams of starch are stirred with 30 grams of water, then poured into 150 grams of boiling water, and stirred and boiled for some time; a good thermometer is now introduced, and the starch mucilage is cooled to and kept at 100° F. on a water-bath. 10 grams of malt-extract dissolved in 10 c.c. of water are stirred into the mucilage, the time being noted, and after one minute, or when the mucilage has become thin, two drops are transferred to one of the vials, which is shaken and placed near a window. This operation is repeated until no coloration, or scarcely any, is produced in the vials; the time occupied indicates the amount of diastase present. Various colorations produced with the iodine solution show the progress of the changes. 1. A greenish-

blue coloration, and after standing the appearance of a blue precipitate indicates *undecomposed starch*. 2. A dark blue solution without a precipitate, *soluble starch*. 3. A purple solution shows that the *quantity of soluble starch equals that of the dextrin and sugar*. 4. A red colour points to the predominance of *dextrin or sugar*, according to depth, the redness increasing with the former. 5. No colour, or scarcely any colour, indicates completion of the change. This plan of procedure is adopted in the experiments with diastase described below. A good malt-extract will convert its own weight of starch at 62° F. within 40 minutes, at 100° F. within 10 minutes, and at 150° F. within 3 minutes, or it will convert five times its weight of starch in 40 minutes at 100° F., or eight times that amount in 90 minutes. Moreover, an extract of this strength will digest the following boiled amylaceous articles:—Potatoes, 4 parts in 3 minutes, 16 parts in 15 minutes; rice, 4 parts in 10 minutes; bread, 4 parts in 9 minutes, 16 parts in 45 minutes; sago, 4 parts in 12 minutes, 8 parts in 30 minutes. The *albuminoïds* are determined by shaking in a tall graduated cylinder 80 parts of a cold saturated solution of picric acid with 20 parts of malt-extract until the extract is dissolved; the precipitate is allowed to settle, and after 24 hours its height is read off. Each division represents 1 per cent. by weight of nitrogenous matter dried at 212° F. The quantity ought to be on an average from 3 to 3.25 per cent. These determinations are sufficient to pronounce an extract good or worthless. The *dextrin*, *sugar*, and *glycerol* can be determined in the following manner:—2 to 5 grams of extract are mixed with 20 grams of dry clean sand, and then dried and weighed, the loss is *water*. The dried mixture is transferred to a percolating tube supported on a small wire stand; the whole is dried and weighed, then percolated with ether, and the residue is dried and weighed; the loss is the *resin*. Percolation of this residue with a mixture of 2 volumes of absolute alcohol and 3 volumes of ether removes the *glycerol*, whilst the *sugar* is removed by subsequent exhaustion with strong alcohol. Treatment with hot water dissolves away the *dextrin* from the albumin; and finally the latter may be destroyed by igniting the sand, which on cooling ought to weigh the same as it did at the beginning of the operation.

The author has made several experiments to study the action of acids, alkalis, and alcohol on diastase. The quantities employed in each experiment were 5 fluid ounces of starch-paste containing 100 grams of starch with 100 minims of saliva, or 100 minims of malt-extract dissolved in 100 minims of water. The malt-solution was prepared fresh every day from the same sample of malt-extract, and was tested to secure a uniformity of diastatic power; it had an acid reaction. The saliva was collected from a number of persons, adults and children, and was tested from time to time; it was always neutral. The starch-paste was heated to and kept at or about 100° F. on a water-bath, the reagent was added and mixed well in, and finally the malt-solution or saliva. The tests were made with the iodine solution as described above, and the observations recorded in the following manner:—

100 minims of	Per cent. reagent.	Colour 1. After minutes.	Colour 2. After minutes.	Colour 3. After minutes.	Colour 4. After minutes.	Nearly colour- less. After minutes.	Remarks.
Extract of malt .....	—	—	—	1	2	7	} Relative diastatic power of malt-extract and saliva.
Saliva .....	—	—	—	4	6	14	
Extract of malt and HCl .....	—	—	—	1	—	2	} Diastatic power of both much increased.
Saliva with HCl .....	—	—	1	5	8	10	
Extract of malt with HCl .....	—	—	—	—	—	—	} Diastatic power com- pletely arrested.
Saliva with HCl .....	—	—	—	—	—	—	
Extract of malt + acetic acid .....	—	—	—	—	1	2	} Power more than doubled.
Saliva and acetic acid .....	—	—	—	1	4	6	
Extract of malt and acetic .....	—	1	2	3	6	—	} Good result with malt. Action of saliva arrested in 2 hours.
Saliva and acetic acid .....	60	120	—	—	—	—	
and so on.							

With a further increasing quantity of acetic acid, the power of malt-extract gradually decreases, until it is arrested when  $1\frac{1}{2}$  per cent. acid is exceeded. With lactic acid,  $\frac{1}{20}$  per cent., the action of both malt-extract and saliva is much increased, especially in the case of saliva; with  $\frac{1}{10}$  per cent., the malt increased, the saliva retarded;  $\frac{1}{5}$  per cent. is favourable to malt, but fatal to saliva; and  $\frac{1}{2}$  per cent. lactic acid stops nearly all diastatic action of the malt-extract.  $\frac{1}{10}$  per cent. of a mixture of 1 part hydrochloric acid, 2 parts lactic acid, and 8 parts acetic acid proves very favourable to the action of both malt and saliva, whilst  $\frac{1}{5}$  per cent. of this mixture is favourable to the malt only. Leaving out the lactic acid in the mixture caused a diminution of diastatic action of both.  $\frac{1}{20}$  per cent. of caustic soda totally destroys the action of saliva, whilst the malt is rendered inactive by  $\frac{1}{10}$  per cent. Alkaline carbonates act less energetically.

Alcohol has only a slight influence on diastatic action, and its action is more marked with saliva or neutral malt-extract. The effect of wines and spirits on diastatic power seems to depend on the proportion the amount of acid present bears to the quantity of starch and malt-extract or saliva; so that when the proportion of acid is large and the quantity of starch and diastase small, the action is very sluggish or stops altogether. This is more evident in the case of saliva than with malt-extract. For example—

	Alcohol p.c.	Acid p.c.	Starch p.c.	Extract p.c.	Saliva p.c.	Colourless in minutes.
Extract of malt with wine	1.5	0.125	3.46	1.73	—	5
" " " "	2.56	0.214	2.9	1.45	—	5
" " " "	5.5	0.460	1.5	1.5	—	{ Colour 2. After 60 mins.
Saliva " " "	1.5	0.125	3.46	—	3.46	45
" " " "	2.56	0.214	2.9	—	2.90	{ Colour 1. After 60 mins.
Malt with whisky .....	13.33	0.0231	2.31	2.31	—	7
Saliva " .....	13.33	0.0231	2.31	—	2.31	4

D. A. L.

**Contribution to a Knowledge of Rye Grain.** By E. EGGER (*Dingl. polyt. J.*, 249, 425).—By subjecting the fruit of rye, which is generally of a greyish-brown colour, to close examination, the author detected shades varying from yellow to dark brown, whilst the grain in some instances exhibited a bluish-green coloration. Under the microscope, some of the gluten cells showed a dark blue colour. Dilute hydrochloric and sulphuric acids change the blue to red, and dilute solutions of alkalis give a yellow colour, which acids do not reconvert into red. By pulverising and sifting the grain, and treating the residual bran with alcohol acidified with hydrochloric acid, a pink extract is obtained. D. B.

**Formation of Alcohol in the Fermentation of Bread.** By V. MARCANO (*Compt. rend.*, 97, 1070—1071).—A leaven, known in France as *levain de chef*, made by mixing potatoes, yams, &c., cooked by steam, with water and flour, yielded on distillation an amount of alcohol equivalent to 54.7 c.c. of absolute alcohol per kilogram of leaven. The solid residue consisted of cellulose with very little starch, and the liquid was saturated with dextrin.

A similar result is obtained on distilling bread paste just before it is put in the oven. These facts show that in the tropics the formation of alcohol at the expense of starch is a constant and regular phenomenon in the fermentation of bread. C. H. B.

**Alteration of Flour.** By BALLAND (*Compt. rend.*, 97, 651—652).—Wheat contains a ferment which appears to exist in the neighbourhood of the embryo. This ferment has the properties of organised ferments, is insoluble, and withstands a temperature of 100° when dry, but is destroyed by boiling water. It is active only in presence of heat and moisture, a temperature of 25° being most favourable to its development. When the wheat is carefully ground, the greater part of the ferment is left in the bran, its proportion in the flour being smaller the more carefully the latter is dressed. If the grinding is too rapid or violent, a larger quantity of the ferment passes into the flour, hence the liability to alteration of flour which is said to be *échauffée*. This can be avoided by grinding with rollers.

The acidity of old flour is not the cause of the disappearance of gluten, but is the result of it. The gluten appears to exist as such in wheat in the same manner as starch, and is not a product of the action of water on a glutenogen. In stored flour, the gluten retains all its properties, but the action of the ferment is retarded by the absence of water. On adding water and warming, its activity is restored. The addition of oatmeal to army flour, although advantageous on account of its nutritive properties and cheapness, renders the flour much more liable to alteration. This might however be prevented by keeping the flour and oatmeal separate, and only mixing them when required for use. C. H. B.

**Acceleration of the Oxidation of Drying Oils.** By A. LIVACHU (*Compt. rend.*, 97, 1311—1314).—When a drying oil, previously treated with litharge or finely divided metallic lead (*Abstr.*, 1883,

p. 757), is agitated with a solution of zinc sulphate, all the lead is precipitated from the oil, but the latter now holds zinc in solution. By using manganese sulphate, copper sulphate, &c., in this way, every trace of lead is removed from the oil, but the lead is replaced by manganese, copper, &c. If an oil charged with lead will dry in 24 hours when spread out in a thin layer on glass, it will dry completely in five or six hours if charged with manganese, in 30 to 36 hours with copper, zinc, or cobalt, and in more than 48 hours with nickel, iron, chromium, &c.

It is more convenient to use the solid finely powdered salt in place of a solution, since the latter forms an emulsion with the oil. In fact, treatment with metallic lead and a solid sulphate may take place simultaneously, but in this case the oil will contain some lead in addition to the other metal.

Although solidification of a drying oil charged with manganese takes place in five or six hours when spread out in thin layers, the solidification of thick layers requires a long time, even though the protecting pellicle which forms on the surface is continually removed. Oxidation is more rapid at a higher temperature, but with thick layers a long time is required for complete solidification, even under these conditions.

A temperature of 50–60° accelerates the oxidation of drying oil, partly because the oil becomes more fluid, and partly because the oxygen is more active at a higher temperature.

When a manganiferous oil is dissolved in an equal volume of benzene, and agitated with air in a closed vessel, rapid absorption of oxygen takes place, especially at a temperature of 40–50°. If the air is continually renewed, so as to furnish the oxygen required for the maximum oxidation of the oil, the liquid becomes thick, and on distilling and separating the solvent a liquid is obtained which solidifies on cooling to a very dry and perfectly elastic solid. It is evident that by limiting the oxidation a series of products of varying viscosity can be obtained intermediate between the original oil and the solid formed by maximum oxidation. The last product is characterised by its remarkable elasticity, and its absolute insolubility in water, alcohol, and ether. It is almost instantly saponified by potash in the cold, and on subsequent separation of the fatty acids it is found that the solid fatty acids have undergone no alteration, whilst the liquid fatty acid has almost completely disappeared, and has been converted into viscous products, characterised by their solubility in water and by the various salts which they form.

C. H. B.

**American Milk.** By E. H. JENKINS (*Bied. Centr.*, 1883, 528–530).—The author gives the following milk analyses:—



	Jersey cows.			Guernsey cows.			Average of six cows.
	From six cows, Jersey.	From five cows, Ayrshire.	From six cows, native.	1.	2.	3.	
Water.....	85·28	87·15	86·43	85·02	82·85	84·82	85·20
Solid residue .	14·72	12·85	13·57	14·98	17·15	15·18	14·80
Casein .....	3·67	3·20	3·34	4·22	4·51	4·00	4·08
Fat .....	5·21	4·33	4·49	5·00	6·62	5·06	5·23
Sugar .....	4·93	4·60	4·82	4·47	4·57	4·69	4·50
Ash .....	0·91	0·72	0·92	1·29	1·45	1·43	1·17
Daily yield...	21 lb. 3 oz.	21 lb. 4 oz.	22 lb. 9 oz.	—	—	—	—
Density.....	—	—	—	1·0326	1·034	1·0353	—

The author has made over 200 analyses of milk collected from various herds; the average amount of solid residue was 12·40 per cent., with a minimum of 9·8 and a maximum of 14·4; and the average amount of fat was 4·02 per cent. with a minimum of 2·6 and a maximum of 5·6. Only one sample contained less than 10 per cent. of solid residue; five samples between 10 and 10·5 per cent.; six samples between 10·5 and 11 per cent.; 19 between 11 and 11·5; 27 between 11·5 and 12; and 150 samples over 12 per cent. The author is not quite certain that all the samples were unadulterated, and thinks the one with 9·8 total solids must have been. The author holds that milk with a sp. gr. less than 1·029 must be adulterated.

J. T.

**Utilisation of Skim-milk.** By B. FOLKERS (*Bied. Centr.*, 1883, 566).—Practical experiments extending over several years have been made by the author near Jever. Fattening calves did not pay, but for pigs the results were economically satisfactory.

J. T.

**Butter-making.** By W. FLEISCHMANN and BLUNCK-SCHILKOWITZ (*Bied. Centr.*, 1883, 554—557).—Milk requiring to be transported before being skimmed for butter-making, gives a better yield of butter when gently agitated from time to time during cooling, before being placed in transport vessels.

Fleischmann finds that butter made without churn in a kneading machine from very thick cream, has the composition 83—86 per cent. fat, 10—16 per cent. water, 0·2 to 0·8 per cent. protein. The thick cream was produced in a Petersen's machine, and such cream can well be made into butter by kneading. The minimum amount of protein, 0·224 per cent., was found in a sample of butter made from cream that had been passed a second time through the machine along with water.

J. T.

**Preserved Butter.** By W. FLEISCHMANN (*Bied. Centr.*, 1883, 557—559).—Such butter should have 4—5 per cent. salt; more does not help to preserve it, spoils the taste, and adds unnecessarily to the weight. Analyses of 16 samples gave 8·34—13·71 per cent. water,

82.91—87.11 butter fat; 0.44—0.79 protein; 0.36—0.87 soluble nitrogen-free matter; 1.08—6.13 ash and common salt. The author remarks that the state of the protein and nitrogen-free organic matter is of more importance than the amount; for if the protein be already in a state of decomposition owing to defective preparation, the butter will not keep, even if little be present. The author finds that sour cream makes as good preserved butter as sweet cream, although this has been denied.

J. T.

**Insoluble Fatty Acid in Goat's Butter.** By C. JEHN (*Arch. Pharm.* [3], 21, 262).—A fatty acid insoluble in water was isolated from goat's butter in the following way:—5 grams of the pure butter fat were saponified with 2 grams of potassium hydroxide and 50 c.c. of alcohol, the solution was evaporated to a syrup, diluted with 100 c.c. of water, and decomposed with hydrochloric acid. The fatty acid was washed with boiling water and dried. The butter fat contained about 87 per cent. of this acid. Goat's butter and cow's butter are thus shown to yield the same quantity of insoluble fatty acids.

W. R. D.

**Blumenthal's Prepared Rennet.** By SCHMÖGER (*Bied. Centr.*, 1883, 852).—This preparation is sold in the solid or liquid form; the solid contains 0.87 per cent. of water, 96.01 ash (principally NaCl, and 3.12 per cent. of organic matter, of which 1.06 is albuminoid). At 35°, this solid, when dissolved, curdles about 80,000 parts of milk, whilst the liquid preparation curdles 8,600 at 35°, and contains 1.83 per cent. organic matter and 13.48 per cent. of ash.

E. W. P.

**"Rennet" Ferment from the Seeds of *Withania Coagulans*.** By A. S. LEA (*Chem. News*, 48, 261—262).—It was noticed that both the fruit and aqueous extract of the seed capsules of *Withania coagulans* coagulated milk. This discovery is of great importance, as the introduction of the cheese-making industry into India depends on finding a vegetable substitute for the ordinary animal rennet, since the natives will not purchase cheese made with the latter. The author has experimented on this vegetable "rennet." The seeds were separated from extraneous matter, the cases, stalks, soil, &c., by crushing and sifting. Then equal weights of the seeds were extracted for 24 hours with equal volumes of water, 5 per cent. sodium chloride solution, 2 per cent. hydrochloric acid, and 3 per cent. sodium carbonate solution, respectively. Equal volumes of each of these extracts in an acid, alkaline, or neutral condition, were added to equal volumes of milk, and heated to 38°. The milk coagulated rapidly with sodium chloride and carbonate extracts, but much more slowly with the other two. Subsequent experiments show that the 5 per cent. salt solution extract is the most active. The ferment is also soluble in glycerol, and closely resembles animal rennet. The ferment is destroyed by boiling, by filtering the solution through animal charcoal, or by treating it with finely powdered kaolin. Alcohol precipitates the ferment from its solutions, but the precipitate, when redissolved, still retains its coagulating properties. A very small quantity of ferment suffices to coagulate milk, large quantities simply

hasten the change. If neutral or alkaline ferment solutions are added to neutral milk, a normal clot is formed, with neutral or faintly alkaline reaction, thus showing that the coagulation is not due to the formation of acid by the ferment. The curd is not a mere precipitate, but a true clot, resembling in appearance and properties that formed by animal rennet. All the extracts of the seeds are deep brown in colour, which, however, is unimportant, as the colouring matter remains chiefly in the whey, the curd being white. Extracts may be made up to contain 15 per cent. salt, and these may be treated with 4 per cent of alcohol without apparently impairing the coagulating activity to any appreciable extent, in fact such a preparation corresponds very closely in activity with the commercial solution of animal rennet; it is therefore probable that extracts of this vegetable "rennet" will be prepared for keeping, but how long these will remain active time alone can show. The ferment has been tried in cheese-making, and, from the results, it would seem that the seeds of *Withania* can be used successfully as a substitute for animal rennet.

D. A. L.

**Cheese from Skim-milk and Foreign Fat.** By X. A. WILLARD and others (*Bied. Centr.*, 1883, 552).—The well-skimmed milk, according to Willard, is intimately mixed at 54° with 1½ per cent. lard at the same temperature in a mixing machine; the so-called *lard-cream* is thus formed, which is then made into cheese with rennet. Such cheese is largely produced near Little Falls, U.S.A.

Griffiths gives analyses of such American cheese purchased in London, as follows:—

	I.	II.	III.	IV.
Water .....	23·49	28·20	26·55	31·81
Casein .....	36·21	37·01	35·58	36·10
Fat .....	34·92	30·18	33·85	28·68
Ash .....	5·24	4·51	3·90	3·40
	99·86	99·90	99·88	99·99

A little arsenic was found in the rind of I and IV, possibly added to keep off insects! Starch was not found.

It is said that olive-oil, and even cotton-seed oil, is largely used instead of lard in several American establishments.

J. T.

**New Coal-tar Dyes.** (*Dingl. polyt. J.*, 249, 350—355, and 383—389).—The firm, late Meister, Lucius, and Brünig (Ger. pat., 22,545, 2nd Sept., 1882) obtain a yellow dye, consisting of dinitronaphthol-monosulphonic acid by the simultaneous action of nitrates and nitrites in acid solution on naphthylaminetrisulphonic acid. It is advantageous to prepare the  $\alpha$ -naphthylaminetrisulphonic acid by first converting the naphthylamine into the monosulphonic form, and then further sulphonating by treatment with fuming sulphuric acid and neutralising with milk of lime, by which the calcium salt is obtained. Naphthylamine, treated with fuming sulphuric only, gives small quantities of the trisulphonic compound.

The firm, late Brönnner of Frankfort-on-the-Main (Ger. pat., 22,547, July 5, 1882), convert the  $\beta$ -naphtholmonosulphonic acid into two new  $\beta$ -naphthylaminesulphonic acids for the preparation of dyes. The monosulphonic acid is produced by Schäffer's method (*Annalen*, **152**, 296). The ammonia salt of this acid is treated under pressure at  $180^\circ$  with calcium hydroxide, or calcined soda and water: the resulting mass is dissolved in hot water and acidified, when the  $\beta$ -naphthylaminemonosulphonic acid separates out. The ammonium salt may be replaced by the corresponding sodium salt, which gives good results when heated with soda and ammonium chloride. An easily soluble  $\beta$ -acid remains in the mother-liquor which is obtained by neutralising with soda, evaporating to dryness, and boiling with alcohol; the acid separates out from the acidified alcoholic solution on cooling. The  $\beta$ -naphthylaminemonosulphonic acid thus obtained dissolves less easily in alcohol than the easily soluble sulphonic acid obtained from  $\beta$ -naphthylamine and fuming sulphuric acid. The diazo-compounds of the first give, with  $\alpha$ -naphtholmonosulphonic acid, a beautiful reddish-blue dye; the corresponding compounds of the second acid give a blood-red dye, strongly tending to brown. By combining the diazo-compounds of both acids with phenol, hydroxy-phenols, and naphthols, their ethers and sulphonic acids, a new series of beautiful dyes are obtained.

W. Harmsen (Ger. pat., 22,707, Sept. 9, 1882) describes a new method for the preparation of yellow, orange, and red dyes, by mixing diazotised bases with aromatic hydroxy-acids and a  $\beta$ -hydroxynaphthol-sulphonic acid. The hydroxy-acids, when mixed with equal molecular weights of diazotised bases, yield dyes whose colours deepen from yellow to red with increase in the carbon present. The carboxyl-group of the hydroxy-acids remains unchanged in the new compounds, so that they still act as acids, decomposing carbonates and even forming salts. The new dyes, which by constitution are hydroxyazocarboxylic acids, dissolve in alcohol, giving bright colours, whilst their alkali salts are soluble in water, and give fast colours on wool as well as on silk. To prepare the dyes, equal molecular weights of diazotised bases and of the sodium salt of an aromatic hydroxy-acid are mixed and rendered alkaline with soda, and the filtered solution is treated with common salt to precipitate the dye in a flocculent form. As the sodium salt of the dye derived from naphthylamine is only slightly soluble in water, it is converted into the sulphonic compound by treating the dry free acid with sulphuric acid, sp. gr. 1.8 at  $160^\circ$ , and the deep blue solution is poured into water, whereon the sulphonic acid separates out. This is dissolved in soda-lye, and treated with common salt, when the sodium salt separates out. This compound is more soluble than the salt directly prepared from the hydroxy-acid, and also possesses stronger dyeing power. The other dyes can be similarly treated by using fuming sulphuric acid instead of the ordinary acid.

*Brown Dyes from Chrysoidine and Diazo-compounds.*—The Aniline Manufacturing Company of Berlin (Ger. pat., No. 22,714, November 8, 1882) remark that when diazotised sulphanilic acid or other diazotised amido-acids are used instead of diazobenzene chloride for the preparation of chrysoidine from metaphenylenediamine, chrysoidinsulphonic

acids, chrysoïdincarboxylic acid, &c., are obtained whose alkali salts are soluble in water. The chrysoïdine and the derived acids just mentioned now take a second molecule of a diazotised base or amido-acid, and yield dyes of the type of phenylenediaminediazobenzene,  $(C_6H_5.N_2)_2.C_6H_4.(NH_2)_2$ , by which the yellow to yellowish-red colour of the chrysoïdine becomes brownish. Usually the dyes prepared from the basic chrysoïdines and diazo-compounds are insoluble in water, but soluble in alcohol. To render these dyes soluble, they are converted into sulphonic acids, and salts of these acids are employed; or the chrysoïdine may be acted on with the salt of a diazo-compound or a diazotised amido-acid, or the chrysoïdine itself can be treated with a diazoted amido-acid.

E. Nölting and E. v. Salis (Ger. pat., No. 22,268, August 31st, 1882) describe new yellow, orange, and brown dyes obtained from the sulphonic acids of nitrated secondary and tertiary aromatic amines which contain two aromatic and one fatty radical. They are obtained by sulphonating the corresponding nitramine, or by the action of aromatic halogen nitro-compounds on aromatic amido-sulphonic acids. Halogen-compounds in which the nitro-groups hold the ortho- or para-position with reference to the halogen, but the meta-position with reference to each other, act readily on amines; whilst under the action of hydrochloric acid, a secondary or tertiary nitramine is formed. The nitramines so obtained are dyes which as yet have not found practical application owing to their slight solubility and other unfavourable qualities; they, however, yield useful dyes if converted into sulphonic acids.

The aromatic halogen nitro-compounds further act on the sulphonic and carboxyl-derivatives of the amines and yield soluble dyes.

The following dyes appear to be of importance technically:—Trinitrodiphenylaminesulphonic acid, which, as well as its salts, form yellow crystals, soluble in water, especially if hot, and dyes silk and wool yellow directly in an acid bath. Tetranitronaphthylphenylsulphonic acid, which is very similar to the foregoing in its properties, but gives a yellowish-brown dye. Lastly the compounds obtained by acting with picryl chloride, chlorodinitrobenzene, and chlorotetranitronaphthalene on amidazomonosulphonic acid, amidazodisulphonic acid, and phenylamidazobenzenesulphonic acid. Orange and brown dyes are thus obtained, which in acid bath dye wool and silk directly.

*Safranin Dyes.*—R. Nietzki has investigated this series of dyes (Abstr., 1883, 731). Witt proposes a method of preparation (*Jour. Chem. Ind.*, 1882, 255) by oxidising a mixture of 1 mol. paraphenylenediamine with 2 mols. aniline, by which the first member of this series of dyes is obtained.

*Phenosafranin*, first obtained by Witt, is prepared by the oxidation of 2 mols. aniline with 1 mol. paraphenylenediamine or of equal molecular weights of aniline and paradiamidodiphenylamine. This dye is not very different in tint from its homologues the safranines of commerce, but is characterised by the great facility with which its salts crystallise out. The chloride forms cantharides-green needles, slightly soluble in cold water, easily soluble in hot, and having the composition  $C_{18}H_{15}N_4.HCl$ . The sulphate forms long steel-blue

needles. *Diethylsafranine* is obtained by oxidising in the presence of 2 mols. aniline, diethylparaphenylenediamine prepared from nitrosodiethylaniline. This dye has a magenta-red colour, its chloride crystallises in beautiful glittering green needles. The platinochloride forms green needles also, which, dried at  $100^{\circ}$ , have the composition  $2C_{16}H_{14}N_4Et_2, H_2PtCl_6$ . If a mixture of 1 mol. paraphenylenediamine with 1 mol. diethylaniline and 1 mol. aniline be similarly oxidised, a compound is obtained isomeric with and very similar to the above. Although both these compounds give green sulphates, they do not afford green diazo-compounds. *Tetretethylsafranine* is obtained by oxidising a mixture of equal molecular weights of diethylparaphenylenediamine, diethylaniline, and aniline; this dye has a much more violet tint than the foregoing. It forms a very soluble chloride, and a less easily soluble double chloride with zinc, which crystallises beautifully. The dye is not sufficiently permanent when exposed to light. Bindschedler describes the preparation of *dimethylphenylene-green*,  $2C_{16}H_{19}N_3, HCl, ZnCl_2$ , also *tetramethylphenylene-safranine*; its nitrate,  $C_{22}H_{22}N_4, HNO_3 + H_2O$ , is brownish-violet, and easily crystallisable; also *dimethylphenylene-safranine*, a magenta-red dye,  $C_{20}H_{18}N_4$ , and analogous compounds.

All the safranines are decolorised by reducing agents. Pure phenylene-safranine,  $C_{16}H_{14}N_4$ , reduced with ferrous ammonium sulphate in an atmosphere of hydrogen, was found to take up 4 atoms of hydrogen in passing to the leucophenylene-safranine. The safranines may be represented by the general formula  $C_nH_{2n-22}N_4$ .

J. T.

**Fixation of Aniline Dye-stuffs by means of Metallic Sulphides.** (*Dingl. polyt. J.*, 250, 183.)—Balanche was the first who utilised certain metallic sulphides as mordants for aniline dyes. The sulphides of zinc and tin, when deposited on cotton, attract magenta, aniline-violet, Bismark-brown, &c., on dyeing. Lüssy has recently experimented with antimony sulphide, and finds that in the dye-bath it absorbs methylene-blue, malachite-green, rosaniline-red, and similar colouring matters. The sulphide process is suitable only for dyeing purposes: the goods are treated with a metallic salt, and then with a soluble sulphide or with a soluble sulpho-salt, and the sulphide is precipitated by an acid. The dyeing is the third operation. In order to apply the sulphide process to steam colours, Schmid recommends the thiosulphate method. Metallic salts, the sulphides of which can be precipitated by means of sodium thiosulphate, are mixed with the latter and the dye-stuff. The mixture is thickened and printed on the fabric. On steaming, the insoluble sulphide is deposited with the dye. Thus it is possible to fix methylene-blue, malachite-green, dimethylaniline-violet, &c., in one operation on the fibre by the aid of the sulphides of cadmium, copper, lead, &c. The resulting colours resist soaping extremely well.

D. B.

**Extracting by Diffusion.** By A. ZWERGEL (*Dingl. polyt. J.*, 249, 307—310).—The author strongly recommends Kohlrausch's method of extracting by employing a battery of diffusers, having employed it for the extraction of log-wood dye. The advantages over the old

method are said to be (a) the liquid to be evaporated is reduced by one-half; (b) the raw material is more thoroughly exhausted; (c) the quality of the extract is essentially improved; (d) the work is simplified and its cost reduced. J. T.

**Preparation of Aluminium Acetate.** By J. ATHENSTADT (*Dingl. polyt. J.*, **250**, 91).—The author separates two-thirds basic aluminium acetate,  $\text{Al}_2(\text{AcO})_4(\text{OH})_2$ , in an amorphous soluble form from concentrated solutions by adding a sufficient amount of sodium sulphate at 30—35°, and stirring the mixture. When freshly prepared, the acetate is perfectly soluble in water and suitable for dyeing. By treatment with lime, a dry mass is obtained which yields a solution of aluminium acetate with separation of gypsum when treated with dilute sulphuric acid. D. B.

**Aluminium Thiocyanate Free from Iron.** By G. STEIN (*Dingl. polyt. J.*, **250**, 36).—Stork and Strobel having introduced aluminium thiocyanate as a substitute for the acetate for alizarin steam colours, it is important in purchasing this article to ascertain whether iron is present or not. Commercial samples of aluminium thiocyanate are invariably contaminated with a greater or less proportion of iron which is contained in the materials used for its preparation. The dissolved iron is mostly present in the form of ferric thiocyanate, which ether dissolves with a red colour. It is possible to extract all the iron from aluminium thiocyanate by means of this solvent; as, however, ether is miscible with the thiocyanate, it is necessary to expel it from the extract as rapidly as possible, otherwise sulphur will be separated.

Aluminium thiocyanate is said to produce fuller and redder steam colours when free from iron. Thiocyanates containing iron exhibit streaky colours having a bluer tint. D. B.

**Explosives.** By BERTHELOT (*Compt. rend.*, **97**, 771—772).—A summary of the contents of the author's new work, "Sur la force des matières explosives, d'après la Thermochemie." C. H. B.

**Liquid Extract of Senega.** By H. J. ROSE (*Pharm. J. Trans.* [3], **14**, 169).—This extract has a great tendency to gelatinise and form a precipitate. The author has remedied the evil by using a mixture of alcohol (7 parts), spirit of nitrous ether (2 parts), and water (7 parts), as a menstruum for extraction, and proceeding as directed in the United States Pharmacopœia. D. A. L.

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## General and Physical Chemistry.

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**A New Copper Oxide Cell.** By F. DE LALANDE and G. CHAPERON (*Bull. Soc. Chim.* [2], **40**, 173—176).—A very useful cell, especially for chemical laboratories, can be made by placing a sheet-iron box containing oxide of copper at the bottom of a glass jar. A plate formed by a spiral of thick zinc wire is suspended from the lid of the jar at some distance above the iron box, and the jar is filled with a 30 or 40 per cent. solution of potash. The positive pole is formed by a copper wire coated with caoutchouc passing through the lid of the jar and attached to the iron box. Other forms of this battery may be constructed by taking advantage of the fact that a paste of copper oxide and magnesium oxychloride hardens to a porous solid mass.

W. C. W.

**Electrolysis.** By SCHUCHT (*Zeitschr. Anal. Chem.*, **22**, 485—495).—The author has investigated the separation of a number of metals from their solutions electrolytically. Luckow (*Abstr.*, 1880, 282) has shown that lead is separated from solution, preferably a nitric acid one, as peroxide, or this mixed with hydrated peroxide. It is only from strongly acid solutions that the whole of the lead separates as peroxide; from feebly acid and concentrated solutions the peroxide is mixed with a large proportion of metallic lead. The separated peroxide was found to contain more water when precipitated from a feeble acid solution than from a strongly acid one, the presence of much free alkali also increases the proportion of water. Solutions of thallium resemble those of lead, the metal being separated either entirely as sesquioxide, or mixed with a small proportion of metal, according to the quantity of free acid present. The thallium is separated from alkaline solutions partly as sesquioxide and partly in the metallic state. Silver is precipitated, in the absence of nitrates or free nitric acid, as metal only, whilst, in the presence of the above, a small proportion of silver peroxide,  $\text{Ag}_2\text{O}_2$ , is formed. Solutions of bismuth are decomposed by the current into metal and bismuthic acid, the latter appearing only gradually at the positive pole, whilst the peroxides of the former metals are formed from the commencement of the current. In the electrolysis of ammoniacal solutions of nickel and cobalt, the sesquioxide appears at the positive pole, but its separation is prevented by excess of ammonia; the largest proportion of sesquioxide obtained by the author amounted to 3—3.5 per cent. of the amount of precipitated metal. Manganese is the only metal which is separated exclusively as peroxide from its solutions. The presence of organic acids, ferrous salts, and salts of chromium or ammonium, prevent the formation of the peroxide and the red coloration due to permanganic acid. Selenium and tellurium are readily precipitated by the current, both from acid and alkaline solutions. P. F. F.

**Electrolysis of Sodium Chloride.** By L. NAUDIN and A. BIDET (*Bull. Soc. Chim.*, **40**, 2—14).—With a view of recovering the chlorine



from bleaching liquors the authors have made a study of the electrolysis of sodium chloride with two Daniell's elements coupled for intensity. Four separate factors are to be considered:—1st, the hypochlorous acid; 2nd, the gaseous chlorine dissolved; 3rd, the gaseous chlorine disengaged, constituting the active chlorine; and 4th, the inactive chlorine remaining in combination with the sodium. It was observed that the chlorine disengaged was a function of the time of electrolysis. From the experiments, an empirical equation,  $\frac{\eta^2}{x} = k = 333$ , is deduced, in which  $y$  is the chlorine disengaged, and  $x$  the number of days, *i.e.*, the curve is parabolic. The curves representing the formation of the hypochlorous acid and the dissolved chlorine are in opposite directions, as the former is produced at the expense of the latter. If the ions liberated at the two poles be separated from one another, no hypochlorous acid is formed; after a few days the dissolved chlorine remains constant, while the disengaged chlorine steadily increases; at the end of eighteen days, however, the active chlorine was only about 6 in 273 parts of total chlorine.

V. H. V.

**Electrolysis of Chlorates.** By LIDOFF and TICHOMIROFF (*Bull. Soc. Chim.*, **39**, 508).—The decomposition of the chlorates by the electric current is never complete when carbon poles are used; these diminish in weight, being attacked by the liberated ozone or oxygen, and converted into mellogen as described by Bartoli and Papasogli.

V. H. V.

**Decomposition of Carbon-compounds by the Silent Discharge.** By MAQUENNE (*Bull. Soc. Chim.*, **40**, 60–65).—In this paper a study is given of the decomposition of a few organic substances under various pressures by the silent discharge, and the gases obtained as to their composition are compared with those formed in the decomposition of the same substances at a dull or bright red heat.

All the substances investigated, except benzene, were rapidly decomposed into carbonic oxide and anhydride, hydrogen, and hydrocarbons: the results are appended below.

*Methyl Alcohol.*

Pressure of gas.	Decomposition by the silent discharge.		Decomposition by heat.	
	3–4 mm.	100 mm.	Dull red heat.	Bright red heat.
CO .....	24·3	19·6	23·0	31·7
CO <sub>2</sub> .....	—	—	1·5	0·5
C <sub>2</sub> H <sub>4</sub> and C <sub>2</sub> H <sub>2</sub>	4·3	0·9	9·4	3·8
CH <sub>4</sub> .....	5·1	36·7	34·4	18·3
H <sub>2</sub> .....	20·4	42·8	31·7	54·7

There were also produced non-volatile resinous products, which escaped analysis, and were dissolved in the excess of the alcohol.

*Ethyl Alcohol.*

Pressure of gas.	Decomposition by the silent discharge.		Decomposition by heat.	
	2 mm.	100 mm.	Dull red heat.	Bright red heat.
CO <sub>2</sub> .....	2·2	0·5	0·5	0·5
CO .....	11·0	14·7	22·1	26·4
C <sub>2</sub> H <sub>4</sub> and C <sub>2</sub> H <sub>2</sub> .....	14·0	1·1	23·5	13·7
C <sub>2</sub> H <sub>6</sub> .....	30·1	21·6	13·8	13·6
H <sub>2</sub> .....	42·6	62·1	40·1	45·8

*Acetic Acid.*

Pressure of gas.	Decomposition by the silent discharge.	
	2 mm.	100 mm.
CO <sub>2</sub> .....	20·7	9·6
CO .....	33·9	44·2
C <sub>2</sub> H <sub>4</sub> and C <sub>2</sub> H <sub>2</sub> .....	2·4	0·3
CH <sub>4</sub> .....	38·5	11·5
H <sub>2</sub> .....	4·5	34·4

The first products of the reaction are probably carbonic anhydride and methane, which subsequently act on one another to form carbonic oxide and hydrogen.

*Acetone.*

Pressure of gas.	Decomposition by the silent discharge.		Decomposition by heat.	
	50 mm.	100 mm.	Dull red heat.	Bright red heat.
CO <sub>2</sub> .....	1·1	0·6	1·2	0·6
CO .....	40·0	42·1	39·5	36·0
C <sub>2</sub> H <sub>4</sub> .....	3·5	2·9	7·0	3·3
C <sub>2</sub> H <sub>6</sub> .....	29·7	30·0	22·4	21·8
H <sub>2</sub> .....	25·7	24·4	22·9	38·3

*Methyl formate* was selected in order to compare the results of its decomposition with those of its isomeride acetic acid.

Decomposition by the silent discharge.	Decomposition by heat.	
	Red heat.	Bright red heat.
CO <sub>2</sub> .....	3·2	2·3
CO .....	61·8	56·0
C <sub>2</sub> H <sub>4</sub> .....	1·3	0·5
CH <sub>4</sub> .....	5·8	5·5
H <sub>2</sub> .....	28·7	35·7

From these results it is evident that the decomposition effected by the silent discharge and by heat are strictly comparable.

V. H. V.

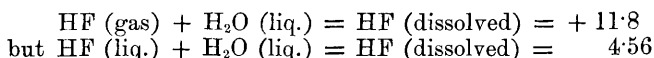
**Boulier's Pyrometer.** By C. LAUTH (*Bull. Soc. Chim.*, **40**, 108—110).—Hitherto all attempts to construct a pyrometer for estimating

very high temperatures, such as those attained in the porcelain manufacture, have been unsuccessful; for this purpose Boulier has constructed a pyrometer consisting of a thin copper cylinder several centimeters in length; one end is closed, the other terminates in two tubes, one of which is connected with a reservoir of water, the other is joined to a thermometer. In order to make an observation, the thin copper tube is introduced in the furnace whose temperature is to be ascertained, and a current of water allowed to circulate from the reservoir. The water in the cylinder is heated by contact with the hot air or flame, and the rise of temperature marked by the thermometer at the exit. In order to ensure the regular circulation of the water, an electric balance is introduced into the copper vessel, which, at the least interruption, stops the water flow. At present this apparatus has only been used for relative and not for absolute differences of temperature.

V. H. V.

**Thermochemical Study of Hydrofluoric Acid.** By GUNTZ (*Bull. Soc. Chim.*, **40**, 54—57).—In this memoir, are given the determinations of the heats of solution in water of gaseous and liquid hydrofluoric acid of various degrees of concentration.

The heat of solution of the gaseous acid was found for one equivalent—



The heat of volatilisation of hydrofluoric acid is the difference between these values  $= 11\cdot8 - 4\cdot56 = 7\cdot22$ .

In order to determine the heat of dilution of hydrofluoric acid, a certain quantity of solution containing a known quantity of the anhydrous acid was added to 400 equivalents of water. The results are appended below—

	Heat disengaged.
HF anhydrous added to 400 H <sub>2</sub> O.....	4·56
HF + 5H <sub>2</sub> O .....	2·05
HF + 1·67 H <sub>2</sub> O .....	0·72
HF + 2·25 .....	0·45
HF + 6·5.....	0·1

These results can be represented by the empirical equations,  $Q$  = heat of dilution—

$$\text{For } n = 5 \text{ to } n = 2 \dots\dots\dots Q = \frac{1\cdot3}{0\cdot13 + n} \text{ (I).}$$

$$,, \quad n = 2 \text{ to } n = 10 \dots\dots\dots Q = \frac{1\cdot3}{0\cdot13 + n} - 0\cdot1 \text{ (II).}$$

Equation (I) is that of a hyperbola asymptotic to the axis of the abscissa and parallel to the axis of the ordinates; equation (II) is also that of a similar hyperbola, the ordinates of which are diminished by 0·1. These results seem to indicate the existence of a definite hydrate, HF, 2H<sub>2</sub>O, and thus confirm the conclusions of Bineau, who

obtained a hydrate of this composition on the distillation of the aqueous acid.

It is further noticeable that the dilution of the acid containing more than 2 mols.  $\text{H}_2\text{O}$  does not produce a sensible evolution of heat; in this point, hydrofluoric differs from hydrochloric, hydrobromic, and hydriodic acids.

V. H. V.

**Heat of Formation of Fluorides.** By GUNTZ (*Compt. rend.*, 97, 1483—1486).—*Ammonium Fluoride*.— $\text{NH}_3$  diss. +  $\text{HF}$  diss. =  $\text{NH}_4\text{F}$  diss., develops + 15.2 cal. Taking Favre's value for the heat of solution of ammonium fluoride, it follows that  $\text{NH}_3$ , gas, +  $\text{HF}$ , gas, =  $\text{NH}_4\text{F}$ , solid, develops + 37.3 cal., and  $\text{NH}_3$ , gas, +  $\text{HF}$ , liquid =  $\text{NH}_4\text{F}$ , solid, develops 30.1 cal. These values are somewhat lower than the corresponding values for potassium, as is the case with other acids.

*Barium Salt*.— $\text{BaO}$  diss. +  $2\text{HF}$  diss. =  $\text{BaF}_2$  diss., develops + 34.8 cal., and  $\text{BaH}_2\text{O}_2$ , solid, +  $2\text{HF}$ , gas, =  $\text{BaF}_2$ , solid, +  $2\text{H}_2\text{O}$ , solid, develops + 71.4 cal. This value is affected by the solubility of the fluoride, and is somewhat too low.

*Strontium Salt*.— $\text{SrO}$  diss. +  $2\text{HF}$  diss. =  $\text{SrF}_2$  diss., develops + 35.8 cal., and  $\text{SrH}_2\text{O}_2$ , solid, +  $2\text{HF}$ , gas, =  $\text{SrF}_2$ , solid, +  $2\text{H}_2\text{O}$ , solid, develops + 71.8 cal. This value is affected by the partial solubility of the fluoride, but not to such a great extent as in the case of barium.

*Calcium Salt*.— $\text{CaO}$ , diss. +  $2\text{HF}$ , diss. =  $\text{CaF}_2$ , solid, develops + 37.2 cal., and  $\text{CaH}_2\text{O}_2$ , solid, +  $2\text{HF}$ , gas, =  $\text{CaF}_2$ , solid, +  $\text{H}_2\text{O}$ , solid, develops + 66.6 cal.

A comparison of the heats of formation of the fluorides, chlorides, and sulphates of the alkalis and alkaline earths, shows that in the case of sodium, potassium, and ammonium, the heat of formation of the fluoride is less than that of the chloride; in the case of barium, the difference is much smaller, whilst in the case of strontium and calcium the heat of formation of the fluoride is greater than that of the chloride. The heats of formation of sodium, ammonium, potassium, and barium sulphates, are greater than those of the corresponding fluorides; in the case of strontium, the difference is very small, and in the case of calcium the heat of formation of the fluoride is slightly greater than that of the sulphate.

C. H. B.

**Heat of Formation of Fluorides.** By D. TOMMASI (*Compt. rend.*, 98, 44—45).—The heats of formation of the alkaline fluorides recently determined by Guntz agree very closely with the values calculated by the author's law of thermochemical constants. This agreement, however, does not obtain in the case of calcium, barium, and strontium fluorides, a result due to the fact that these compounds are insoluble in water, whilst the author's law applies only to soluble substances.

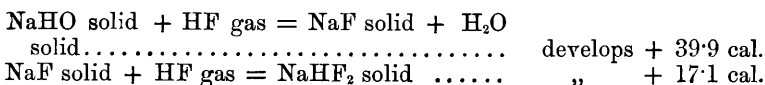
C. H. B.

**Heat of Formation of Fluorides.** By BERTHELOT (*Compt. rend.*, 98, 61—63).—A criticism of Tommasi's claim to the law of thermochemical constants.

C. H. B.

**Sodium Fluorides.** By GUNTZ (*Compt. rend.*, **97**, 1558—1560).

—The heat of formation of these compounds is deduced from their heats of solution and neutralisation. The heat of solution of NaF is 0·6 cal. at 12°, and that of NaHF<sub>2</sub> is -6·2 cal. Combining these data with Thomsen's values for the heats of neutralisation, it follows that—



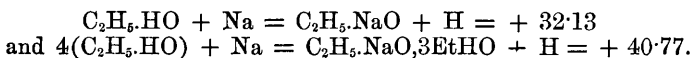
These values are somewhat lower than the corresponding values for potassium, and the heat of formation of sodium fluoride is lower than that of the chloride and sulphate, as in the case of the corresponding potassium compounds. On the other hand, the heat of formation of sodium hydrogen fluoride is greater than that of sodium hydrogen sulphate, although the difference is not so great as with the potassium salts.

C. H. B.

**Heat of Formation of Alcoholates.** By DE FORCRAND (*Bull. Soc. Chim.* [2], **40**, 177—183).

—Three alcoholates of sodium can be prepared by the action of metallic sodium on alcohol and distilling the product in a vacuum. C<sub>2</sub>H<sub>5</sub>.NaO,3EtHO, is obtained in colourless needles if the reaction takes place at the ordinary temperature, but if the alcohol is heated at 70° the product has the composition C<sub>2</sub>H<sub>5</sub>.NaO,2EtHO; C<sub>2</sub>H<sub>5</sub>.NaO may be prepared by heating either of the preceding compounds at 200° in a current of hydrogen. These compounds are easily decomposed by moisture and by oxidation. They generally contain one-thirteenth of an equivalent of sodium hydroxide.

The heat of solution in water of each of these compounds is respectively +13·47, +10·46, and +12·34. From these numbers the heat of formation of C<sub>2</sub>H<sub>5</sub>.NaO may be calculated to be +17·35, starting from Na<sub>2</sub>O or +0·25 from NaHO, when O = 8.



The heat of formation of NaHO by the action of Na on H<sub>2</sub>O is +33·3.

The heat of solution of C<sub>2</sub>H<sub>5</sub>.NaO in a large excess of alcohol is +12·56.

*Barium alcoholate* generally contains one-tenth to one-fifth of an equivalent of baryta.

The heat of formation for the compound by the action of an equivalent of alcohol on an equivalent of barium monoxide is +7·24, and on the hydroxide = -0·84.

A small quantity of water added to the alcoholic solution of barium ethylate throws down a precipitate of barium hydroxide.

W. C. W.

**Heats of Combustion of Ketones and Carbonic Ethers.** By W. LOUGUININE (*Compt. rend.*, **98**, 94—97).

	Per 1 gram.	Per gram-molecule.
Diethyl ketone .....	8569.0 cal.	736,934 cal.
Dipropyl ketone .....	9244.5 „	1,053,873 „
Diisopropyl ketone.....	9172.4 „	1,045,654 „
Methyl hexyl ketone .....	9467.1 „	1,211,789 „
Dimethyl carbonate .....	3774.34 „	339,691 „
Diethyl carbonate .....	5442.8 „	642,250 „

The difference between the heats of combustion of the isomerides dipropyl ketone and diisopropyl ketone is only 0.8 per cent. of the total value, a difference within the error of experiment. This affords further confirmation of the law that isomerides of the same chemical function develop approximately the same quantities of heat on combustion.

The difference between the heats of combustion of diethyl ketone and dipropyl ketone is 316,939 cal. for  $2\text{CH}_2$ , or 158,470 for  $\text{CH}_2$ . In the case of dipropyl ketone and methyl hexyl ketone, the difference is 157,916 cal. for  $\text{CH}_2$ . These values are similar to those obtained in other homologous series.

In the case of the two carbonates, the difference for  $\text{CH}_2$  is 151,280 cal. for  $\text{CH}_2$ , or slightly less than in other homologous series.

On comparing the heats of combustion of dimethyl carbonate and dimethyl ketone, which differ only by  $\text{O}_2$ , it is found that the introduction of these two atoms of oxygen into the molecule diminishes the heat of combustion by 84,310 cal., or 42,155 cal. for each atom of oxygen. A similar comparison between diethyl carbonate and diethyl ketone gives a difference of 47,342 cal. for each atom of oxygen. The difference between these two values for the influence of oxygen is not much greater than the error of experiment.

C. H. B.

**Glycollide.** By DE FORCRAND (*Bull. Soc. Chim.* [2], **40**, 57—60).—Various methods have been prepared for the preparation of glycollide: (I) distillation of tartaric acid (Dessaignes); (II) distillation of glycollic acid (Heintz); (III) heating hydrated sodium monochloracetate (Kekulé). But in all these processes water is eliminated simultaneously with the formation of glycollide; as these substances tend slowly to reunite, there is established a final equilibrium between the glycollide formed and the glycollic acid reproduced; the yield is thus materially diminished. Further, the final product is contaminated with substances of composition intermediate between glycollic acid and glycollide. The most practical method of preparing glycollide consists in heating dry sodium monochloracetate.

From the following data, the heat of hydration of glycollide can be calculated:—

Heat of neutralisation of glycollic acid by soda .....	= + 13.6
Heat of solution of solid glycollic acid.....	— 2.76
Heat of transformation of glycollide to sodium glycollate .....	+ 11.96

Therefore

$\text{C}_2\text{H}_2\text{O}_2$  (solid) +  $\text{H}_2\text{O}$  (liquid) =  $\text{C}_2\text{H}_4\text{O}_3$  (solid) = + 1.12  
and

$\text{C}_2\text{H}_2\text{O}_2$  (solid) +  $\text{H}_2\text{O}$  (solid) =  $\text{C}_2\text{H}_4\text{O}_3$  (solid) = - 0.31

Thus the reaction with liquid water is exothermic although the heat evolved is very small; these results are in accordance with the transformation of glycollide into glycollic acid.

Glycollide is thus the thermic analogue of lactide, but stands in marked contrast with such anhydrides as sulphuric; whilst on the other hand, Berthelot's experiments tend to show that the conversion of dissolved carbonic anhydride into carbonic acid would be an endothermic reaction.

V. H. V.

**Disodium Glycollate.** By DE FORCRAND (*Bull. Soc. Chim.*, **40**, 104—106).—In the course of a study of the heat of formation of different salts of glycollic acid, it was observed that the addition of excess of soda to neutral sodium glycollate caused an appreciable development of heat, which varied with the degree of dilution of the liquid.

In order to isolate the disodium glycollate, the existence of which was suspected from the above phenomenon, a syrupy solution of caustic soda was added to a supersaturated solution of sodium glycollate, and the resultant liquid evaporated in a vacuum; very deliquescent small needles of a salt  $\text{C}_2\text{H}_2\text{O}_3\text{Na}_2 \cdot 2\text{H}_2\text{O}$  separated out. Its heat of formation can be expressed by the equation  $2\text{NaHO}$  (sol.) +  $\text{C}_2\text{H}_4\text{O}_3$  (sol.) =  $\text{C}_2\text{H}_2\text{Na}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  (sol.) = + 31.42, or if the anhydrous salts be formed,  $2\text{NaHO}$  (sol.) +  $\text{C}_2\text{H}_4\text{O}_3$  (sol.) =  $\text{C}_2\text{H}_2\text{Na}_2\text{O}_3$  (sol.) +  $2\text{H}_2\text{O}$  (sol.) = + 24.76.

V. H. V.

**Crystallisation of Substances at High Pressures.** By E. JANNETAZ, NEEL, and CLERMONT (*Bull. Soc. Chim.* [2], **40**, 51—54).—Spring has recently succeeded in transforming pulverulent amorphous substances into crystalline masses by means of a pressure of 5000 atmospheres. These experiments have been repeated by Friedel with a different form of machine, but with negative results. This paper deals with some further experiments in this direction, especially as regards the relation of the propagation of heat in substances, and their structure, whether natural or artificial. The following substances were subjected to pressures of 6000—8000 atmospheres:—

Metals. Finely powdered tin, copper, lead, zinc, and iron; antimony and bismuth; Darcel's alloy.

Sulphides of lead and zinc.

Chlorides of sodium, lead, and mercury.

Precipitated magnesia and alumina.

Pulverised silica, chalk.

All these substances were agglutinated into solid masses, but displayed no signs of crystalline, but of schistose form.

The experiments of Sorby, Tyndall, and Daubrée have established that clays take a schistose form when subjected to pressure, and the cleavage plane is perpendicular to the direction of the pressure. One

of the authors has also proved that the plane of propagation of heat is identical with that of cleavage. On examining the metallic masses obtained by compression, it was found that they possessed the thermic property characteristic of a schistose structure.

V. H. V.

**Crystallisation of Substances under Pressure.** By W. SPRING (*Ber.*, 16, 2833—2835).—A reply to Jannettaz, Neel, and Clermont (preceding Abstract).

**Dissociation.** By ISAMBERT (*Compt. rend.*, 98, 97—100).—The author applies Berthelot's general formula of dissociation to cases in which a gas is produced, and introduces a term representing the mechanical work effected. He deduces various relations between the temperatures, specific heats, and maximum tensions, and shows that they are in agreement with his observations on the dissociation of ammonium dihydrosulphide and ammonium carbonate.

C. H. B.

**Combustion of Explosive Gaseous Mixtures.** By MALLARD and LE CHATELIER (*Bull. Soc. Chim.*, 39, 572—581).—A continuation of the author's researches.

The irregularity of the velocities of propagation cause determinations of mean velocities between any two given points to be but of a secondary interest; for the mean value varies not only between two successive, but also between the same points in different experiments. By means of a photographic method, the velocities of propagation of explosion of mixtures of carbon bisulphide with oxygen or nitric oxide have been studied. These observations show that there are several distinct phases or periods of propagation.

(I.) *Uniform Movement.*—The flame advances regularly and uniformly.

(II.) *Vibratory Movement.*—The flame advances in oscillations whose amplitude and duration vary very rapidly.

(III.) *Wave of Explosion.*—It is projected suddenly towards the end of the tube.

(IV.) *Extinction.*—In certain cases, the flame is suddenly extinguished, and all combustion ceases.

1st Phase. The velocity of this uniform movement is very constant in different experiments with tubes of the same diameter, but of different lengths; with tubes of different diameters, the velocity diminishes with decrease of diameter. The following may be stated as a general result: on first ignition of an explosive mixture the combustion is propagated with a uniform velocity less than 30 metres per second.

2nd Phase. The further progression of the flame is marked with oscillatory movement. This phase is always noticeable in slow burning mixtures such as carbon bisulphide and nitric oxide; it is not so distinct with more explosive mixtures. The duration of successive vibratory movements varies from 0.025 to 0.0034 second; they stand to one another in a simple arithmetical progression. Their amplitude is greater the longer the period of the vibration; in some cases it was



found to be enormous. The brilliancy of the flame varies during the successive phases of the same vibration; in the recoil, it is less than in the advance. The mechanism of this vibratory movement is analogous to that of musical flames.

3rd Phase. The explosive wave has been minutely studied by Berthelot and Vieille; the mixtures of carbon bisulphide with oxygen and nitric oxide displayed this phenomenon, but its mode of production varied in the two cases; with the former, it developed itself very rapidly, succeeding almost immediately the phase of uniform movement; with the latter, it succeeds the period of long vibration.

4th Phase. With mixtures of carbon bisulphide and nitric oxide in tubes of 0.1 in. diameter, the amplitude of the flame oscillations increases very rapidly, then the combustion ceases. This result is analogous to that obtained by Schützenberger in his study of the combustion of limited mixtures of hydrogen and oxygen, when he observed an extinction of combustion at one of the nodes of vibration of the eudiometric tube, *i.e.*, the point of the greatest oscillation of the flame.

In conclusion, a general summary of the various observed phenomena is given, with especial reference to the explosive wave. If the hypothesis of Berthelot and Vieille be correct, then its course of propagation can be explained; for the ignition of the first section of gas tends to increase its volume, and to produce an immediate compression of the sections in front, followed by a recoil. This alternating compression and recoil travels from section to section with the velocity of sound; they tend temporarily to increase or decrease the temperature of each successive section, but the increase is not sufficient to ignite the inflammable mixture, nor the decrease sufficient to extinguish it, if ignited.

V. H. V.

**Prout's Hypothesis.** By M. GERBER (*Bull. Soc. Chim.*, **39**, 562—572).—Prout's hypothesis, supported by a considerable weight of evidence, and by *à priori* probability, is admitted generally in principle, although the value of the fundamental unit is quite unknown. If the elements be divided into four classes, characterised by their dominant atomicity, there is for each class a common factor, integer multiples of which include all the sufficiently known atomic weights. These common factors are in simple relation to one another. The table below contains the four factors—

	O = 15.96.	O = 16.
$d_1 = \frac{1}{3}\text{H} \dots\dots$	0.7673	0.7692
$d_2 = 2\text{H} \dots\dots$	1.995	2.0
$d_3 = \frac{5}{16}(\frac{5}{4})\text{H} \dots$	1.5586	1.5625
$d_4 = \frac{5}{4}\text{H} \dots\dots$	1.247	1.25

In the original memoir, the atomic weights from Clarke's calculations are compared with the values calculated from the integer multiples of these several factors.

In the course of discussion the simplicity of the multiples of these factors is noticed in certain groups of elements such as O, S, Fe, or Li, K, Rb, but a complexity in other groups as Cl, Br, I.

In some cases an element can equally be classed in two of the four divisions, for the terms of the progression  $nd_4$  coincide frequently with those of the progression  $nd_3$ , as, for example,  $4d_3=5d_4$ ; zinc or mercury can be classed similarly in the second or fourth division.

Further, the stoichiometrical determinations will decide whether these relations are merely fortuitous or whether they form a part of a wider generalisation.

V. H. V.

**Relation between Molecular Weight and Velocity of Evaporation of Liquids.** By C. SCHALL (*Ber.*, 16, 3011—3014).—If equal volumes of benzene and water are distilled consecutively in the same apparatus, and with as nearly as possible equal rates of ebullition, different amounts by weight of the two liquids distil over in a given time. The amount of benzene in a rough experiment was about double the amount of water. In a more exact trial, the liquids were heated in their respective vapours, and the lengths of time required for the evaporation of equal volumes was observed. These observations were reduced by means of the sp. gr. of the liquids at their boiling points to equal weights, and the time of evaporation then calculated. The values obtained for two comparable substances are nearly inversely proportional to their molecular weight. If  $m$  and  $m'$  are the molecular weights, and  $t$  and  $t'$  the time of evaporation for each, then  $m : m' = t' : t$  and  $m = m' \frac{t'}{t}$ . Thus he obtained—

Benzene.		Chloroform.	
Boiling point.....	79.2°	Boiling point.....	61.5°
Sp. gr.....	0.8136	Sp. gr.....	1.4048

*Length of Time of Evaporation of Equal Volumes.*

	Benzene.	Chloroform.	Calculated for equal weight of benzene.
I. ....	12.7 min.	14.3 min.	8.25 min.
II. ....	12.95 „	14.5 „	8.4 „
III. ....	12.3 „	14.0 „	8.28 „

By means of the above formula he obtains for the molecular weight of chloroform : I, 119.64; II, 120.25; III, 115.88.

The author also finds that the ratio of the volumes of liquids distilled in equal time is equal to the ratio of their atomic volume at the boiling point. The ratio of benzene to chloroform in experiment I is 1.126 : 1, and taking the atomic volume of benzene at 95.94, that calculated for chloroform in this way is 85.2, whilst Schiff found 84.65. The author has obtained equally good results with benzene and carbon bisulphide, but less satisfactory with other liquids. With some compounds of equal molecular weights, such as amylalcohol and ethyl acetate, he obtained equal lengths of time of evaporation for equal weights of substances. He intends continuing his work on this subject.

In comparing the latent heat of vaporisation of liquids in relation

to their molecular weight, it has been found in seven compounds that the former decreases as the latter increases.

	Latent heat of vaporisation.	Mol. wt.
Water .....	536·67	18
Alcohol .....	214·3	46
Acetone.. .....	129·72	58
Ethyl acetate .....	90·7	74
Carbon bisulphide ....	83·7	76
Chloroform .....	61·0	119
Carbon tetrachloride ..	46·5	154

Also that certain substances may be grouped, from the fact that the products of the latent heat of vaporisation into the molecular weight gives a number nearly constant for members of a group. Thus water and alcohol form a group; and acetone, chloroform, and carbon tetrachloride, a second.

A. B.

**Lecture Experiments.** By V. MEYER (*Ber.*, 16, 2998—3001).—For the purpose of showing *the action of light on an explosive mixture of chlorine and hydrogen*, the author fills jars 25 cm. high and 35 mm. wide with the mixture, and closes them with paper covers; one is left colourless and others coloured violet and yellow by means of spirit varnish and aniline colours. On igniting a large quantity of magnesium-dust in a Bunsen burner, the gas in the colourless and violet jars instantly explodes, but that in the yellow jar does not, and may be fired with a burning chip. A fourth colourless jar may be kept to show *photochemical induction*, for whilst with sufficient magnesium-dust the explosion takes place instantly, on exposing the mixture to burning magnesium wire, several seconds elapse before the gases combine.

*Preparation of Chlorine Monoxide, Cl<sub>2</sub>O.*—This gas can be prepared by passing a regular stream of dry chlorine over commercial yellow mercuric oxide (previously heated for some time at about 400°) in a horizontal glass tube,  $\frac{1}{2}$  m. long, cooled in ice. The chlorine monoxide which is formed is collected by displacement in a vertical narrow cylinder, and can be exploded by throwing in flowers of sulphur or with a light, or if collected in a strong test-tube and closed with an india-rubber stopper by heating the bottom of the tube. The explosion although accompanied with development of light and formation of smoke, is not dangerous.

The author, with the aid of a drawing, describes a form of funnel which he uses for protecting liquids from dust, during evaporation on the water-bath. The rim of the inverted funnel is turned in so as to form a circular trough, in which the condensed vapours are collected. By this means the water-bath and the floor of the draught cupboard are protected from acid and other droppings.

A. B.

## Inorganic Chemistry.

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### Ebullition of Liquid Oxygen and Solidification of Nitrogen.

By S. WROBLEWSKI (*Compt. rend.*, **97**, 1553—1555).—When oxygen, liquefied by means of the apparatus previously described, is allowed to evaporate rapidly by sudden removal of the pressure, it does not solidify like carbonic anhydride, but a white crystalline residue is deposited on the bottom of the apparatus. This residue disappears as the temperature rises, but whether it is solid oxygen or is due to some impurity in the oxygen (which was made from potassium chlorate and manganese dioxide) has not been determined.

Determinations by a thermoelectric method indicate that the temperature produced by the rapid ebullition of oxygen under these conditions is about  $-186^{\circ}$ . Nitrogen gas cooled at this temperature and then allowed to expand forms a snow-like mass of crystals of considerable size.

Hydrogen compressed under about 150 atmos. at  $-136^{\circ}$  and then allowed to expand suddenly, shows no signs of liquefaction.

C. H. B.

**Density of Liquid Oxygen.** By MENGES (*Compt. rend.*, **98**, 103—104).—Wroblewski's method of determining the density of liquid oxygen is not satisfactory, because it is assumed that the quantity remaining gaseous is proportional to the total amount of the gas, which is improbable.

If the tube of a Cailletet apparatus is partly immersed in a cold liquid whilst the remainder of the tube is surrounded by a liquid at the ordinary temperature, then—

$$Q = vd + Vx,$$

where  $v$  is the volume of the liquid portion,  $V$  that of the gaseous portion,  $d$  the density of the liquid, and  $Q$  the total weight. If another experiment is made with a shorter length of the same tube in the cold liquid, matters being so arranged that the volume of the liquefied gas is the same as in the first experiment, then—

$$Q = v_1d + Vx + V_1d_1,$$

where  $V + V_1$  is the total volume of the gaseous part,  $v_1$  the volume of the liquid, and  $d_1$  the density of the gas in that part of the tube near the mercury. The pressure and the temperature of this part of the tube being known, the value of  $d_1$  can be calculated, and the two equations yield the expression—

$$d = \frac{V_1d_1}{v - v_1}.$$

C. H. B.

**Duration of the Solidification of Superfused Sulphur.** By D. GERNEZ (*Compt. rend.*, **97**, 1477—1480; see also this vol., 389).—In the course of the experiments described in former papers, the

author observed the formation of crystals of sulphur, the time of solidification of which, whatever its absolute value, is always intermediate between that of the octohedral and that of the prismatic variety. These crystals are long prisms with a nacreous lustre, and, instead of increasing equally in all three directions, as in the case of the prisms and octohedra, they increase far more rapidly in the direction of the longitudinal axis than in the direction of the transverse axes. In order to produce all three varieties under the same conditions, a graduated U-tube is filled with superfused sulphur and the formation of octohedra is started in one limb. As soon as the surface of the sulphur in this limb has become solid, a glass thread or platinum wire is passed down the other limb to the bend of the tube, and is *gently* tapped against the walls of the tube. The formation of the nacreous prisms begins from the points which have been struck, and proceeds more rapidly than the growth of the octohedra. After a short time, a crystal of prismatic sulphur is dropped into the second limb, and the formation of prisms at once begins and proceeds very rapidly, eventually extending round the bend into the limb in which the octohedra were first formed. If the wire is struck too forcibly against the sides of the tube, the formation of the ordinary prisms ensues. The nacreous prisms are obtained by a *slight* cooling at any point in superfused sulphur; if dropped into a tube of the superfused substance, they give rise exclusively to similar crystals, which devitrify somewhat rapidly when cooled to the ordinary temperature, but which can be broken in the liquid without changing their form.

Observations on the formation of these nacreous crystals similar to those made with the other two varieties, show that their time of solidification is very short when the temperature of superfusion is very low, but gradually increases as this temperature approaches the melting point of the sulphur. The time of solidification depends on the time during which the sulphur was heated above the melting point, and also on the time during which it has remained in a superfused condition. When heated to different initial temperatures, the nacreous crystals behave like the other two varieties; the time of solidification increases very considerably if the sulphur has been heated up to about  $170^{\circ}$ , but diminishes if the initial temperature has been much higher. These results were obtained with sulphur which had not previously been fused. Experiments with sulphur which had been converted into the nacreous prisms several times, or which had been previously solidified in octohedra or in prisms, confirm the author's conclusions as to the instability of ordinary prismatic sulphur and the influence of time on the modifications which the sulphur is capable of undergoing.

C. H. B.

**Time of Existence of Thiosulphuric Acid in Aqueous Solution.** By H. LANDOLT (*Ber.*, 16, 2958—2967).—The method of observation was to mix solutions of sodium thiosulphate and an acid such as oxalic acid at the same temperature, and by means of a stop watch to note the time which elapsed before the appearance of the sulphur precipitate. The author found that with a solution which remained unaltered for 30 seconds, his error of observation did not

exceed 1.5 seconds, and usually was a fraction of a second. He also found that different organic or inorganic acids; an excess of sodium thiosulphate or of acid in the same quantity of water; or the gross quantity of solution used, made no difference in the time of existence. The difference in time depends on the relative quantity of water to thiosulphuric acid formed, and on the temperature of the solutions. As the result of many observations, he finds that the time increases exactly in proportion to the dilution of the solutions at constant temperature, or in other words to the number of parts by weight of water to one part by weight of thiosulphuric acid formed; and that the higher the temperature the more rapid the decomposition. The accelerating influence of heat, however, diminishes as the temperature is raised, and this diminution of the time of existence for a difference in temperature, of say  $10^\circ$ , is more observable the greater the proportion of water by weight to thiosulphuric acid. An equation has been evolved to give the time of existence ( $E$ ) for any temperature ( $t$ ) between  $10^\circ$  and  $50^\circ$ , and for any solution in which the parts by weight of water ( $n$ ) to one part by weight of thiosulphuric acid are between 51 and 279; and the results of 40 tabulated observations are in accordance with it:—

$$E_1 = n(0.6428 - 0.02553t + 0.000272t^2).$$

Neither light nor electricity have any influence on the decomposition, but alcohol increases the time of existence very materially, 50 per cent. of alcohol in place of 50 per cent. of water prolonging in one case the time of existence from 64 seconds to 510 seconds.

A. B.

**Sulphur Salts derived from Phosphorus Trisulphide.** By G. LEMOINE (*Compt. rend.*, **98**, 45—48).—When an excess of phosphorus trisulphide is allowed to act on a very dilute solution of sodium hydroxide at  $0^\circ$ , and the solution is evaporated in a vacuum, hydrogen sulphide is given off, and acid sodium phosphite is alone obtained. If, however, the sodium hydroxide is in excess, and the filtered liquid is evaporated in a vacuum over sulphuric acid and phosphoric anhydride, in about five months it deposits quadratic prisms of the composition  $\text{Na}_2\text{S}, 5\text{H}_2\text{O}$ . After another month, the compound  $\text{P}_2\text{O}_3, 2\text{Na}_2\text{S}, 5\text{H}_2\text{O}$  or  $\text{P}_2\text{OS}_2, 2\text{Na}_2\text{O}, 5\text{H}_2\text{O}$  separates out; its solution gives an orange-yellow precipitate with lead acetate. After four months a third compound,  $\text{P}_2\text{OS}_2, 3\text{Na}_2\text{O}, 4\text{H}_2\text{O}$ , separates. Its solution gives a slightly yellowish-white precipitate with lead acetate. Another different preparation gave a salt of the composition  $\text{P}_2\text{O}_3, 3\text{Na}_2\text{O}, 3\text{H}_2\text{S}, 3\text{H}_2\text{O}$ . The substance  $\text{P}_2\text{OS}_2, 3\text{Na}_2\text{O}, 4\text{H}_2\text{O}$  is interesting because it represents a sulphur derivative of phosphorous acid in which all three atoms of hydrogen have been replaced by a base.

When an excess of phosphorus trisulphide is gradually added in small portions to ammonium hydrosulphide, cooled at  $0^\circ$ , and the liquid allowed to stand about 15 days, white crystals of ammonium phosphite,  $2(\text{NH}_4)_2\text{HPO}_3 + \text{H}_2\text{O}$ , separate out mixed with small quantities of a sulphur compound. If the mother-liquor is evaporated in a vacuum, hydrogen sulphide is given off in large quantities.

and after about 28 weeks the compound,  $P_2O_3 \cdot 2(NH_4)_2O \cdot 3H_2O$ , is deposited. Its solution gives an orange-yellow precipitate with lead acetate. If this salt is dissolved in water, and the solution evaporated in a vacuum, the compound,  $P_2O_3 \cdot 2(NH_4)_2O \cdot 6H_2O$ , separates out. It is evident from this fact that these salts lose hydrogen sulphide very easily. This last compound may be regarded as derived from monothiophosphorous acid,  $P_2O_3 \cdot nH_2O$ , whilst the others are derived from dithiophosphorous acid  $P_2OS_2 \cdot nH_2O$ .  
C. H. B.

**Maximum Solubility of Sodium Sulphate.** By E. PAUCHON (*Compt. rend.*, **97**, 1555—1556).—The heat of solution of a salt in water can be calculated by means of an equation given by Kirchhoff, and in this way it can be shown that the heat of solution of sodium sulphate is at first negative, but changes its sign above  $33^\circ$ . It follows therefore that the crystallisation of the salt below  $33^\circ$  ought to develop heat, and heat should be absorbed at higher temperatures; and this supposition agrees with the facts. It is well known that the salt is hydrated if crystallised below  $33^\circ$ , but anhydrous if crystallised at a higher temperature. Berthelot has shown that in the latter case the heat of solution is negative at low temperatures, and the author finds that it is still negative at  $50^\circ$ .  
C. H. B.

**Action of Bromine and Iodine on Silver Chloride, Bromide, and Iodide.** By P. JULIUS (*Zeitschr. Anal. Chem.*, **22**, 523—525).—On passing a current of air saturated with bromine-vapour over silver iodide contained in a porcelain boat and heated to fusion in a piece of combustion tubing, the whole of the iodide is converted into silver bromide in 10 minutes. On substituting silver chloride for the iodide, the whole of the chloride is converted into silver bromide in 1—2 hours' time. If a current of air saturated with iodine-vapour is passed over fused silver chloride or bromide, these are wholly converted into silver iodide, the change requiring 6—10 hours with the former and 3—4 hours with the latter.  
P. F. F.

**Decomposition of the Acid Phosphates of the Alkaline Earths in Presence of Water.** By A. JOLY (*Compt. rend.*, **97**, 1480—1483).—When a dilute solution of phosphoric acid is mixed with an equivalent quantity of a solution of calcium or barium hydroxide, so that the liquid contains equal equivalents of acid and base, the solution is acid to litmus but neutral to "helianthine." Solutions as dilute as those furnished by lime-water and baryta-water remain neutral when saturation is complete, but if the sides of the vessel are rubbed with a glass rod, or if the liquid is heated to about  $80^\circ$  hydrated dicalcium phosphate is precipitated and phosphoric acid is liberated, the liquid becoming acid to helianthine. In presence of water, the monobasic phosphate first formed is partially decomposed by mechanical disturbance or by elevation of temperature into dibasic phosphate and free phosphoric acid, whilst the remainder of the monobasic phosphate remains in solution. Similar decomposition is produced if a fragment of dibasic phosphate is dropped into the original solution. The proportion of dibasic phosphate precipitated depends on the dilution of the solution, and increases with the con-

centration until, when the latter passes a certain point, a neutral liquid cannot be obtained because the dibasic phosphate is at once precipitated.

When pure calcium carbonate is dissolved in an excess of phosphoric acid and the liquid evaporated in a vacuum, the monobasic phosphate is obtained in transparent rhomboidal lamellæ which have the composition  $\text{CaH}_4\text{P}_2\text{O}_8 + \text{H}_2\text{O}$ , and do not alter on exposure to air: in contact with water at the ordinary temperature these crystals decompose and yield a crystalline precipitate of the composition  $\text{CaHPO}_4 + 2\text{H}_2\text{O}$ . When the same weight of water is allowed to act for some time on increasing quantities of the monobasic phosphate, the amount of phosphoric acid liberated continually increases, and the ratio, R, between the total phosphoric acid and that remaining in combination when decomposition has ceased varies from 1 to 1.5. Beyond the latter limit, any further quantity of the monobasic phosphate dissolves in the acid liquid without decomposition, and the ratio diminishes slightly. On the other hand, if one of the more concentrated solutions containing precipitated bibasic phosphate is diluted with water, the precipitate partly redissolves and R diminishes, and in very dilute solutions tends to unity. A solution containing a given percentage of phosphoric acid can dissolve a certain maximum weight of the monobasic phosphate without decomposition, but if this limit is exceeded decomposition takes place and dibasic phosphate is precipitated. If a dilute solution of this kind is concentrated by evaporation in a vacuum, the ratio R increases, dibasic phosphate is precipitated, and by slow evaporation can be obtained in beautiful crystals. When R reaches its maximum value, 1.5, the monobasic phosphate is in turn deposited and the proportion of free acid in the liquid increases.

If a small quantity of any substance capable of combining with phosphoric acid to form a soluble or insoluble compound (*e.g.*, soda, potash, alkaline acetates, ferric oxide, &c.) is added to one of the acid solutions obtained by the decomposition of monocalcium phosphate in presence of water, equilibrium is destroyed and dibasic calcium phosphate is precipitated.

It is evident from these facts that the decomposition of monobasic calcium phosphate by water is not analogous to the decomposition of antimony and bismuth compounds by the same liquid.

C. H. B.

**Cerite and the Extraction of Cerium, Lanthanum, and Didymium therefrom.** By A. ARCHE (*Monatsh. Chem.*, **4**, 913—925).—Two samples from Trommsdorff were analysed. The analyses add up to 104.26 and 103.29; this is due to the method employed for the decomposition of the mineral, viz., fusion with sodium and potassium carbonate: the silica so obtained when treated with hydrofluoric acid left a residue containing cerium, lanthanum, and didymium. If the mineral be decomposed by sulphuric acid, then the silica obtained is pure.

After allowing for the small quantities of copper, bismuth, molybdenum, and sulphur, as also carbonic anhydride and the corresponding amount of lime, the author expresses the composition by the formula



$(\text{Ce}, \text{La}, \text{Di})_6\text{Si}_5\text{O}_{19} \cdot 2\text{H}_2\text{O}$ . After discussing the several methods proposed to decompose cerite, the following is mentioned as giving the best results. The substance is obtained as an impalpable powder by grinding and washing. The dried cerite powder is well stirred into half its weight of strong sulphuric acid, the mass thickens, heats, and gives off fumes of sulphuric acid. After cooling it is easily crushed, and is then added with constant stirring to 12 or 20 times its weight of ice-cold water. The solution obtained is worked up according to Bunsen's method; the residue, which may contain undecomposed mineral as well as silica, may be again treated with sulphuric acid.

H. B.

**Preparation of Bismuth Free from Arsenic.** **Atomic Weight of Bismuth.** By J. LÖWE (*Zeitschr. Anal. Chem.*, **22**, 498—505).—The author has already pointed out (Abstr., 1272, 329) that bismuth hydroxide, precipitated from a nitric acid solution by means of caustic potash or soda, dissolves in an excess of these reagents in the presence of glycerol. From this solution the whole of the bismuth is precipitated in a finely divided metallic state on adding a sufficient quantity of grape-sugar and boiling. Iron and nickel if present do not dissolve in the alkaline glycerol, whilst arsenic does. The sugar should be added in the cold, so that any silver or copper may be precipitated as metal or suboxide respectively, and filtered off, whilst the bismuth is not separated until the solution is boiled. In this manner bismuth may be obtained perfectly free from arsenic. The author has determined the atomic weight of bismuth by taking a known weight of the metal so prepared, dissolving it in nitric acid, converting the nitrate into oxide by ignition, and then weighing. Taking the atomic weight of oxygen to be 15·96, the author finds that of bismuth to be 207·330, whilst if oxygen = 16, it is 207·845. The previous determinations of the atomic weight of bismuth have been :—

Dumas .....	210·27
Schneider .....	207·995
Lothar Meyer and Seubert .....	206·9—208·2

P. F. F.

**Pure Chromic Sulphate.** By H. BAUBIGNY (*Compt. rend.*, **98**, 100—103).—An aqueous solution of carefully purified potassium dichromate is saturated with hydrogen sulphide, and then heated to boiling. The chromium is completely precipitated as hydroxide, and the solution contains potassium sulphate, thiosulphate, and polysulphide, to the latter of which it owes its yellow colour. The precipitate is carefully washed first with cold and afterwards with hot water, and then consists of chromic hydroxide free from alkalis, and containing only traces of oxysulphur compounds, which have no injurious effect. It is dissolved in the least possible quantity of nitric acid, and the solution heated in order to form the violet salt. A slight excess of dilute sulphuric acid is added, and the violet chromium sulphate is precipitated by alcohol, in which the green variety is soluble. The precipitated salt is rapidly filtered off, re-dissolved in dilute sulphuric acid, again precipitated, and finally purified by repeated solution in water and precipitation by alcohol.

Another method consists in carefully reducing chromic monochlorhydrin with alcohol in such a way as to avoid elevation of temperature, then add the requisite quantity of dilute sulphuric acid, precipitate by alcohol, and purify as above. These are the only methods which yield the perfectly pure sulphate, since this salt obstinately retains traces of free acid even in a vacuum at  $440^{\circ}$ .

The chromic oxide is tested for alkali by heating it at a high temperature in a muffle, treating the ignited substance with dilute nitric acid, and testing the solution for chromic acid by adding a few drops of silver nitrate solution and evaporating to dryness, when red silver chromate is left.

Dichromates, when heated to redness, lose chromic anhydride, which decomposes into oxygen and chromic oxide, the latter being deposited on the sides of the muffle in crystalline lamellæ.

C. H. B.

**Borotungstates.** By D. KLEIN (*Bull. Soc. Chim.*, **39**, 581—589).—A continuation of the author's researches (Abstr., 1881, 23, 24, 224, 879, 880; 1882, 17; 1883, 23, 786).—On boiling a saturated solution of sodium paratungstate with three-quarters of its weight of boracic acid, and precipitating the crude product of the reaction with barium chloride, a barium salt of composition  $10\text{WO}_3 \cdot 2\text{BaO} \cdot \text{B}_2\text{O}_3 + 20\text{H}_2\text{O}$ , is obtained. It crystallises in orthorhombic prisms.

V. H. V.

**Reduction of Molybdenum and Tungsten Compounds.** By O. v. D. PFORDTEN (*Annalen*, **222**, 137—165).—The experimental part of this paper has already been given (Abstr., 1883, 122 and 785). The author tabulates the colours of the oxides of the chromium group in acid solution as follows:—

	Cr = 52.	Mo 96.	W 184.	U 240.
I.	$\text{CrO}$ , blue	—	—	—
II.	$\text{Cr}_3\text{O}_4$ ,* black	—	—	—
III.	—	$\text{Mo}_5\text{O}_7$ { reddish-brown; dil. yellow }	—	—
IV.	$\text{Cr}_2\text{O}_3$ { reddish-violet or green }	$\text{Mo}_2\text{O}_3$ { red or green }	—	$\text{U}_2\text{O}_3$ , dark-red
V.	$\text{CrO}_2$ , brownish-red	$\text{MoO}_2$ { brownish-red; dil. yellow }	$\text{WO}_2$ { reddish-brown }	$\text{UO}_2$ , green
VI.	—	$\text{Mo}_3\text{O}_8$ , blue	$\text{W}_3\text{O}_8$ , blue	$\text{U}_3\text{O}_8$ ,* greenish-black
VII.	$\text{CrO}_3$ , yellowish-red	$\text{MoO}_3$ , colourless	$\text{WO}_3$ , colourless	$\text{UO}_3$ , yellow

The end-products obtained by the reduction with zinc and hydrochloric acid ( $\text{CrO}$ ,  $\text{Mo}_5\text{O}_7$ ,  $\text{WO}_2$ ,  $\text{U}_2\text{O}_3$ ), and also by the chlorination ( $\text{Cr}_2\text{Cl}_6$ ,  $\text{Mo}_4\text{Cl}_{10}$ ,  $\text{WCl}_6$ ,  $\text{U}_2\text{Cl}_{10}$ ), do not quite follow the order of the

\* Not known in acid solution.

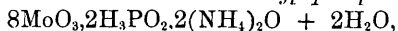
atomic weights of this group. With other reducing agents, however, the results are quite regular.

	H at high temperatures.	HCl.	HI in aqueous solution.	H <sub>2</sub> S.
CrO <sub>3</sub> . MoO <sub>3</sub> .	Metal, easily Metal, easily	Cr <sub>2</sub> O <sub>3</sub> Bluish-green oxide, MoO <sub>3</sub> + MoO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub> Mo <sub>2</sub> O <sub>5</sub> (or MoO <sub>2</sub> I)	Cr <sub>2</sub> O <sub>3</sub> Blue oxide be- tween MoO <sub>3</sub> and MoO <sub>2</sub>
WO <sub>3</sub> .	Metal, but with more difficulty	—	Pale greenish coloration from slight reduction	—
UO <sub>3</sub> . .	UO <sub>2</sub>	—	—	—

The author believes the irregularity in the former case to be due to the varying conditions under which the reactions are necessarily carried out.  
L. T. T.

**Researches on the Complex Inorganic Acids.** By W. GIBBS (*Amer. Chem. J.*, 5, 361—383).—A continuation of the author's previous investigations on this subject (this Jour., 1877, 847; Abstr., 1882, 469, 702; 1884, 161).

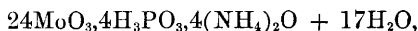
**HYPOPHOSPHOMOLYBDATES.**—*Ammonium hypophosphomolybdate*,



is precipitated on adding hydrochloric acid to mixed solutions of 14:6 acid ammonium molybdate and sodium hypophosphite. It forms colourless prismatic crystals, readily soluble in hot water, the solution being first pale blue, but soon deepening in colour; it dissolves in cold water to a colourless, strongly acid solution, which gives the following reactions:—With thallous nitrate, a white flocculent precipitate; with mercurous nitrate, a canary-yellow precipitate; with argentic nitrate, a nearly white precipitate, which speedily blackens. The following salts give precipitates only after addition of ammonia: barium, strontium, and calcium chlorides, colourless flocculent precipitates, becoming granulo-crystalline after a time; manganese sulphate, a white flocculent precipitate; cupric sulphate, a green flocculent precipitate. On heating the ammonium salt, it blackens, fumes slightly, and melts to a dark blue mass, which gives off a little molybdenum tetroxide when heated to redness.

**HYPOPHOSPHOTUNGSTATES.**—The *Potassium salt*,  $18\text{WO}_3, 6\text{H}_3\text{PO}_2, 4\text{K}_2\text{O} + 7\text{H}_2\text{O}$ , is prepared by mixing a strong solution of hypophosphorous acid with 12:5 acid sodium molybdate solution, dissolving the resulting gelatinous mass in hot water, and adding potassium bromide, when a white crystalline precipitate forms. On recrystallisation, the salt is obtained in small colourless granular crystals, soluble in hot water to a somewhat turbid acid liquid. The solution gives no precipitate with copper salts, even on boiling; a precipitate of silver on boiling with silver nitrate; a white flocculent precipitate with mercurous salts; and a white precipitate of indistinct feathery crystals with barium salts.

PHOSPHOROSO-MOLYBDATES.—*Ammonium salt*,



is obtained by the action of phosphorus acid on 14:6 acid ammonium molybdate as a pale yellow indistinctly crystalline precipitate, insoluble in cold water, very slightly soluble in hot water, readily soluble in alkalis. It decomposes readily when heated, fusing at a low red heat with evolution of fumes of molybdic tetroxide. The following reactions are obtained by boiling the salt with solutions of metallic salts:—Barium chloride forms a fine-grained crystalline salt; silver nitrate, a nearly colourless flocculent substance, which soon darkens, and finally assumes a dull violet colour; mercurous nitrate, a pale yellow flocculent salt; cupric sulphate dissolves the salt to a clear blue liquid.

VANADIO-MOLYBDATES.—*Analytical methods.* The separation and estimation of vanadium and molybdenum present some difficulties, but may be effected by the two following methods:—1. Any vanadium present as dioxide is to be oxidised to vanadic acid by heating it with nitric acid, the solution nearly neutralised by means of an alkali carbonate, and vanadic and molybdic acids precipitated together by means of mercurous nitrate and mercuric oxide; the precipitate is then carefully ignited, and finally heated to redness with a weighed quantity of normal sodium tungstate, the increase in weight on which gives the sum of the weights of the molybdic and vanadic oxides; the weight of the vanadium oxide alone being determined in another portion of the precipitate by heating it in a current of air when all the molybdic oxide is volatilised. Another method is founded on the precipitation of the vanadium as ammonic metavanadate, the vanadium in the precipitate being determined volumetrically. The author mentions incidentally that very good determinations of the vanadium in alkaline vanadates may be effected by precipitation with mercurous nitrate and mercuric oxide, ignition of the precipitate, solution in hydrochloric acid, and titration of the vanadic pentoxide with standard solution of ferrous ammonium sulphate, the end-point being determined by means of potassium ferricyanide.

6:1 *Series*.—The ammonium salt,  $6\text{MoO}_3, \text{V}_2\text{O}_5, 2(\text{NH}_4)_2\text{O} + 5\text{H}_2\text{O}$ , prepared by dissolving molybdic tetroxide in solution of ammonium metavanadate, crystallises in lemon-yellow octohedrons, and is soluble in a large quantity of cold water. It gives a flocculent yellow precipitate with silver nitrate; a bright yellow precipitate with mercurous nitrate; a pale yellow flocculent precipitate with thallous nitrate; and with barium chloride, on standing, a deposit of well-defined octohedral crystals.

8:1 *Series*.—The barium salt,  $16\text{MoO}_3, 2\text{V}_2\text{O}_5, 5\text{BaO} + 28\text{H}_2\text{O}$ , is prepared by adding vanadic pentoxide in small quantities at a time to a boiling solution of acid ammonium molybdate, allowing to cool somewhat, and adding barium chloride, when an abundance of beautiful, well-defined, yellow octohedrons separate.

18:1 *Series*.—The ammonium salt,  $18\text{MoO}_3, \text{V}_2\text{O}_5, 8(\text{NH}_4)_2\text{O} + 15\text{H}_2\text{O}$ , is obtained in pale green tabular crystals by dissolving molybdic tetroxide in a boiling solution of ammonium metavanadate, and allow-

ing it to crystallise. The crystals are decomposed if boiled with water.

**VANADIO-TUNGSTATES.**—The vanadium and tungsten in these compounds can be estimated by methods founded, either on decomposition by boiling with alkalis and precipitation of the vanadium as ammonium metavanadate, or on the evolution of chlorine by the action of strong hydrochloric acid on vanadic pentoxide.

**5 : 1 Series.**—The ammonium salt,  $5\text{W}_2\text{O}_3 \cdot \text{V}_2\text{O}_5 \cdot 4(\text{NH}_4)_2\text{O} + 13\text{H}_2\text{O}$ , crystallises indistinctly in orange-yellow crusts; it is obtained by boiling 12 : 5 ammonium tungstate with solution of ammonium metavanadate.

When the oxides obtained by igniting a mixture of ammonium metavanadate with 12 : 5 sodium tungstate are boiled with water, a greenish-yellow solution is obtained, which takes an orange colour on being boiled with nitric acid, and on standing deposits a sulphur-yellow crystalline substance of the formula  $10\text{WO}_3 \cdot \text{V}_2\text{O}_5 + 22\text{H}_2\text{O}$ . The mother-liquor, from which the preceding acid had separated, gave on evaporation beautiful crystalline needles of an acid having the formula  $18\text{WO}_3 \cdot \text{V}_2\text{O}_5 \cdot 36\text{H}_2\text{O}$ .

A. J. G.

**Manganese Chloro-silicate.** By A. GORGEU (*Compt. rend.*, 98, 107—110).—When a mixture of 20 grams pure manganous chloride and 1 gram precipitated silica is heated at a cherry-red heat for about 45 minutes in a current of moist hydrogen, a regulus is obtained consisting of rhodonite, tephroite, and a chloro-silicate. The latter is decomposed by water, but is only very slowly acted on by alcohol, and the excess of manganous chloride can be removed by means of this latter liquid. The residue is a mixture of the birefractive silicates with large lamellæ, which have brilliant faces, and do not act on polarised light. By careful treatment with a 1—2 per cent. solution of pure nitric acid mixed with a few drops of sulphurous acid, the chloro-silicate can be dissolved out without sensibly affecting the simple silicates. The chloro-silicate has the composition  $\text{SiO}_2 \cdot 2\text{MnO} + \text{MnCl}_2$ , and forms anhydrous crystals, which in all probability belong to the cubic system, but the exact form of which could not be determined. They do not alter when exposed to dry air, but they rapidly absorb moisture from a damp atmosphere and turn brown. When gently heated, the chloro-silicate loses its chlorine in the form of hydrochloric acid, and the manganese is mainly converted into peroxide. Water free from air causes the separation of a neutral hydrated silicate, but in presence of air silica is liberated, and the manganese is converted into peroxide. The chloro-silicate is also decomposed by saturated solutions of carbonic acid and hydrogen sulphide, and by a solution of sodium hydrogen carbonate. The general action of acid and oxidising reagents is similar to that which they exert on the normal silicate, but is more energetic. This chloro-silicate can also be obtained by fusing the normal silicate with an excess of the chloride in a current of dry hydrogen.

When manganous bromide is fused with silica in a similar manner, it yields crystalline lamellæ of similar appearance and properties. Manganous iodide under the same conditions yields the simple sili-

cates, and only forms the iodosilicate in very small quantity. The latter can, however, be obtained by fusing artificial tephroite in a mixture of manganous and potassium iodides.

C. H. B.

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## Mineralogical Chemistry.

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**Occurrence of Diamonds in a Pegmatite in Hindustan.** By CHAPER (*Compt. rend.*, **98**, 113—115).—Not far from Bellary in the Nizam, diamonds occur *in situ*, associated with amorphous corundum, in a pegmatite which also contains epidote. The diamonds are crystallised in octohedra with brilliant faces, but the forms of the crystals are not so distinct as in the case of the South African diamonds. The pegmatite undergoes disintegration and denudation at its outcrop, and the heavy rains wash the *débris* down to lower levels, leaving fresh surfaces of the rock exposed. This explains the fact that from time immemorial the Hindus in this district have found diamonds on the surface of the soil after the rainy season. It seems probable that this rock has furnished the diamonds found in the various alluvial deposits in Hindustan, for it is stated that all these deposits contain “granite,” although the particular granitoid rock is not specified. The irregular distribution and not very frequent occurrence of the pegmatite will explain the facts that the diamonds are generally very rare, and that different deposits vary considerably in their richness. Since the diamond has been formed in a rock so old as pegmatite, it may occur in the various deposits such as grits, quartzites, &c., which have been formed by the denudation of pegmatite, and its occurrence in sedimentary rocks associated with crystallised quartz, &c., does not necessarily prove that it has been developed in a sedimentary paste, or has been formed in the same manner as minerals in veins. It would seem that the diamond has been formed by different methods, for it is not probable that the diamonds in pegmatite and those in the aqueous magnesian breccia of South Africa have been formed in the same way. C. H. B.

**Amalgam from the Friedrichssegen Mine near Oberlahnstein.** By F. SANDBERGER (*Jahrb. f. Min.*, 1884, **1**, Mem., 191—192).—Amalgam having been found to exist at the Friedrichssegen Mine, it occurred to the author to test the specimens of the so-called native silver for mercury. The two specimens examined were purchased from Stürtz in Bonn, and were described as native silver and native copper respectively. Both were situated on white lead ore. In both cases, the mercury reaction was very distinct. B. H. B.

**Native Lead and Minium in Idaho.** By W. P. BLAKE (*Jahrb. f. Min.*, 1884, **1**, Ref., 198, and *Amer. J. Sci.*, **25**, 161).—At the Jay Gould Mine, Alturas Co., Idaho, metallic lead occurs enclosed in

galena. The metal forms rounded masses from  $\frac{1}{8}$  to  $\frac{1}{4}$  in. in diameter, or in reniform bunches. The metal is surrounded by a crust of minium. B. H. B.

**Minerals from Brazil.** By A. KENNGOTT (*Jahrb. f. Min.*, 1884, 1, Mem., 187—191).—This paper contains a crystallographical description of specimens of euclase, topaz, diamond and pyrrhotine, from the province of Minas Geraës, recently presented by C. Heusser and G. Claraz to the mineral collection of the Zürich Polytechnicum. B. H. B.

**Sagvandite.** By H. ROSENBUSCH (*Jahrb. f. Min.*, 1884, 1, Mem., 195—198).—The rock named Sagvandite by Pettersen occurs interstratified in the deeper beds of slate of the Balsfjord group between the lakes Sagvand and Tagvand. The rock consists, for the most part, of an irregular granular mixture of a colourless transparent mineral of the pyroxene group and a rhombohedral carbonate. The microscopic and chemical examination of the rhombic pyroxene prove it to be bronzite, and the carbonate is found on analysis to have the composition indicated by the formula  $9\text{MgCO}_3 + \text{FeCO}_3$ . Small grains and octohedral crystals of chrome-picotite, sp. gr. 4.843, also take part in the composition. Pyrites is met with occasionally. A colourless mica occurs more frequently, and with a certain amount of regularity. Lastly, around the spinelle-mineral, a colourless substance occurs but sparingly, and never independently. The indices of refraction of this substance are about the same as those of zircon or sphene. B. H. B.

**Artificial Reproduction of certain Silicates and Titanates.** By L. BOURGEOIS (*Jahrb. f. Min.*, 1884, 1, Ref., 196—198).—*Wollastonite*.—Equivalent amounts of CaO and  $\text{SiO}_2$  were fused together and cooled. The experiment lasted two days. The crystals obtained were long prisms, frequently twins, with positive double refraction. Sp. gr. = 2.7. The product thus differed from the natural wollastonite. The author is of opinion that calcium silicate is dimorphous, and that a product exactly similar to the natural wollastonite has never yet been obtained artificially.

*Meionite*.—A mixture having the composition  $\text{Ca}_5\text{Na}_2\text{Al}_8\text{Si}_9\text{O}_{36}$ , was fused. The microliths observed on cooling were uniaxial with positive double refraction, and, hence, do not exactly correspond with the natural meionite. By fusing a mixture,  $\text{Ca}_6\text{Al}_5\text{Si}_9\text{O}_{36}$ , the author obtained anorthite and glass.

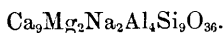
*Gehlenite* was obtained in tetragonal crystals by fusing a mixture,  $\text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10}$ . The author also obtained distinct crystals of gehlenite from mixtures in which the lime was partially replaced by MgO and the  $\text{Al}_2\text{O}_3$  by  $\text{Fe}_2\text{O}_3$ .

*Melilite*.—A mixture of 12 parts of lime to 1 of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , and 9 of  $\text{SiO}_2$ , after fusing and cooling, gave sections which were recognised as biaxial.

Another experiment, in which 2 parts CaO were replaced by MgO, was more successful, tetragonal sections being obtained which optically corresponded to melilite. The same mineral was obtained by fusing a mixture,  $10\text{CaO}$ ,  $2\text{MgO}$ ,  $\frac{3}{2}\text{Al}_2\text{O}_3$ ,  $\frac{1}{2}\text{Fe}_2\text{O}_3$ ,  $9\text{SiO}_2$ .



Very perfect crystals were obtained from a mixture:



When the soda was replaced by potash, melilite was also obtained.

*Garnet*.—Various mixtures corresponding with garnet in composition were fused, but only in one case with success; the mixture,  $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ , giving hausmannite and, probably, spessartine.

*Dichroite*.—A mixture,  $\text{MgO}, \text{Al}_2\text{O}_3, \frac{5}{2}\text{SiO}_2$ , gave a mass of microliths, the optical properties of which corresponded with those of dichroite.

*Rhodnite* was obtained by fusing together  $\text{MnO}_2$  and  $\text{SiO}_2$ . By fusing together 3 parts  $\text{MnO}_2$  and 2 parts  $\text{SiO}_2$ , the author obtained a mixture of tephroite, hausmannite, and rhodonite.

*Sphene and Perowskite*.—A mixture of lime, silica, and  $\text{TiO}_2$ , corresponding with sphene in composition, was fused, but without any satisfactory results. When the elements of melilite were fused with those of perowskite, crystals of the two minerals were obtained. The two minerals were also obtained when melilite was fused with sphene. When the elements of sphene were fused with those of perowskite, crystals of perowskite were obtained together with calcium silicate and a glassy mass.

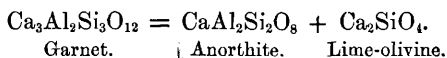
B. H. B.

**Synthetical Mineralogical Studies.** By C. DOELTER and E. HUSSAK (*Jahrb. f. Min.*, 1884, 1, Mem., 158—177).—I. *Garnet*.—The authors have already shown (Abstr., 1884, 401) that garnet, when fused in rocks, gives spinelle, glass and augite. The success of this experiment induced them to study the products obtained when the various varieties of garnet are fused alone. The first experiments soon showed that from fused garnet, garnet is not again formed. The varieties fused were: melanite, pyrope, almandine, and grossular. An experiment lasted 12—14 hours. All the garnets, when fused, were decomposed into other minerals: meionite and melilite, anorthite, lime-olivine, lime-nepheline, iron-glance, and spinelle; the latter appearing when glass occurs. 1. Melanite from Frascati was decomposed into a meionite mineral with positive double refraction, and anorthite, together with a biaxial mineral, probably lime-iron-olivine. 2. Grossular from Rezbanya gave a mineral of the meionite group chemically resembling melilite, with positive double refraction, together with lime-olivine, and very rarely anorthite. 3. Grossular from Wilui gave meionite, some anorthite, iron-glance (?), and a melilite-like mineral. 4. Pyrope from Krimlitz gave anorthite, melilite, and pleonast. 5. Almandine from Zillerthal and the garnet from the granite of Aschaffenburg gave lime-nepheline, melilite, pleonast, and some glass. 6. The brown garnet from Franklin gave anorthite, lime-iron-olivine, and some iron glance. 7. The authors repeated Fouqué's experiment of fusing nepheline and augite; but no melanite was obtained.

The decomposition of garnet into meionite and melilite may be expressed as follows:—



The decomposition into anorthite and lime-olivine :—



II. *Vesuvian*.—The fusion-products of vesuvian are the same as those of garnet, namely: meionite, melilite, anorthite and, perhaps, lime-olivine. Vesuvian from the Rympfischwäng gave meionite, melilite, some anorthite and hausmannite. The green vesuvian from Ala was reproduced; a meionite-like mineral and melilite were also observed. Anorthite was not visible, but a brown mineral belonging to the spinelle-group occurred. Similar results were obtained on fusing vesuvian from Vesuvius. The manganese-holding vesuvian from Ala gave meionite, anorthite, and a mineral probably belonging to the olivine-group.

In these experiments, the variable character of the double refraction of the minerals of the meionite-group is very remarkable. Bourgeois has recently shown (see preceding Abstract) the positive character of the double refraction of artificial meionite. In the fusion-products of garnet and vesuvian, the melilite and meionite minerals show sometimes positive, sometimes negative double refraction; the former being the more frequent. The double refraction of nepheline, artificial or natural, is always negative.

B. H. B.

**The Scapolite Group.** By G. TSCHERMACK (*Monatsh. Chem.*, **4**, 851—888).—The known minerals of this group are crystallographically identical, and are distinguished by their appearance and chemical composition; the numbers and characteristics of the members of this group are not definitely determined. The variations of interfacial angles are very small, the prismatic cleavage is always the same, and the variation of form is also inconsiderable. The crystals have been reported as showing pyramidal and then trapezohedral-hemihedry; owing to the irregularities of the crystals, it is impossible to decide this by mere inspection of the occurring faces. By observing, however, the etching figures produced by hydrofluoric acid, and in a few cases the natural etching figures and raised faces (*vicinal-flächen*) the pyramidal hemihedry is satisfactorily established. The recognised chemical constituents are oxygen, silicon, aluminium, calcium, and sodium; the calcium and sodium appear to replace each other, but no specimens have been found containing only one or other of these two. Potassium often displaces sodium in part; magnesium and iron belong to foreign impurities; water is present in minute quantity only; carbonic anhydride is generally due to admixed calcite, but the author is of opinion that a molecular compound of a silicate and carbonate is occasionally present. Chlorine is also present, and increases with the percentage of sodium and sulphuric acid, but in such small and variable quantity as not to allow of the determination of its mode of occurrence. A table containing five complete analyses is given, as also one of six analyses, showing that as the silica rises from 40 to 62 per cent., the alumina falls from 33 to 22 per cent., the lime from 24 to 5 per cent., whilst the alkalis rise from 2 to 10 per cent.

The chemical resemblance between the scapolite and plagioclase minerals has often been pointed out, and it is here shown that the relation between the silica and the alumina is the same as in the feldspars, viz., as 2 : 1 in the calcium, and as 6 : 1 in the sodium compound. Further, it is shown that the ratio of alumina to lime plus soda is as 3 : 4, differing thus from the ratio in the feldspars, which is 1 : 1. But as before noticed, chlorine is an essential constituent, and its quantity increases with the amount of sodium; taking those analyses showing the most chlorine with but little sulphuric acid, it is seen that the sodium and chlorine are to each other in the ratio 4 : 1. Coupling together these observations, the author infers that the scapolite minerals are composed of an isomorphous mixture of two substances,  $\text{Si}_6\text{Al}_6\text{Ca}_4\text{O}_{25}$  and  $\text{Si}_9\text{Al}_3\text{Na}_4\text{O}_{28}\text{Cl}$ , which he designates by the names meionite and marialite, the composition of these most nearly corresponding with the above formulæ. Having regard to the composition and isomorphism of anorthite and albite, the author writes the above formulæ:—Meionite,  $3(\text{Si}_4\text{Al}_4\text{Ca}_2\text{O}_{16}) + 2\text{CaO}$ ; marialite,  $3(\text{Si}_6\text{Al}_2\text{Na}_2\text{O}_{16}) + 2\text{NaCl}$ .

The scapolite minerals form an indefinite series of intermediate products; they may, however, be arbitrarily divided into three groups containing (1) 40·31 to about 48 per cent. silica, viz., meionite, and among other opaque varieties wernerite; (2) 48 to 56 per cent. (about) of silica, viz., mizzonite and scapolite, &c., as opaque varieties; (3) 56 to 63·83 per cent. of silica, viz., marialite and riponite, &c., which are opaque.

Tables are given comparing the numbers obtained in thirty analyses with those calculated from the above formulæ; the two series of numbers compare very favourably. The approximate densities are calculated to be, meionite 2·764, and marialite 2·540. The relationships between the composition of these two minerals and plagioclase, epidote, muscovite, and kaolin are pointed out, as also the formation of pseudomorphs after these minerals or after the scapolite minerals.

H. B.

**Decay of Rocks Geologically Considered.** By T. STERRY HUNT (*Jahrb. f. Min.*, 1884, 1, Ref., 225, and *Amer. J. Sci.*, 26, 190—213).—Recent geological studies point to the antiquity and universality of the weathering of crystalline rocks. The decay took place, to a great extent, in pre-Cambrian times. The products have frequently remained undisturbed either by being covered by overlying strata, or by being in positions sheltered from erosion. Although the weathering process is continuous, it has been very insignificant since the glacial period, on account of the relatively small time which has since elapsed. This weathering process has furnished the material for the formation of the sedimentary rocks, and of the crystalline limestones, iron-ore beds, &c. The rounded masses left during the process of decay constitute the boulders of the drift, and the similar masses in pre-glacial conglomerates. The outlines of the eroded regions of crystalline rocks were also determined by sub-aërial decay.

B. H. B.

**The More Recent Eruptive Rocks of Elba.** By W. R. NESSIG (*Jahrb. f. Min.*, 1884, 1, Ref., 232—233).—The eruptive rocks of the

central portion of the Island of Elba are quartz-porphyrries, and may be classed as granitic porphyries, porphyritic microgranites, and compact quartz-porphyrries. In spite of their apparently eocene age, they have nothing in common with the rhyolites. Tourmaline occurs only in the granitic porphyries and microgranites. Zircon occurs widely distributed in all the rocks with the exception of the porphyritic microgranites. Twin crystals of zircon occur but rarely. The author is of opinion that the porphyries are independent rocks, and have nothing to do with the Capanne granite. B. H. B.

**Hypersthene Andesite.** By C. W. CROSS (*Jahrb. f. Min.*, 1884, **1**, Ref., 227—229).—The author finds that an apparently typical augite-andesite from the Buffalo Peaks, Colorado, contains hypersthene as its chief pyroxenic constituent. The hypersthene was isolated by Fouqué's method, and gave on analysis the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	Total.	Sp. gr.
51·157	2·154	18·360	0·363	3·812	24·251	100·097	3·307

The interesting results obtained by the author from the investigation of the Buffalo Peaks rocks induced him to examine carefully a series of European augite-andesites. He arrived at the conclusion that the greater part of the pyroxene corresponds optically and structurally with the hypersthene of the Buffalo Peaks rocks. B. H. B.

**Chemical Composition of the Phonolites of Hegau.** By C. F. FÖHR (*Jahrb. f. Min.*, 1884, **1**, Ref., 233—235).—Analysis I gives the composition of the phonolite of Hohentwiel; sp. gr. 2·41; 54·8 per cent. soluble in hydrochloric acid. II gives the results of the analysis of the yellow natrolite (sp. gr. 2·171) from the fissures in the rock. III, the natrolite (sp. gr. 2·183) from the phonolite of Hohenkrähen. IV, the hornblende needles (sp. gr. 3·414) of the rock. V, the phonolites of Gennersbohl; 39·19 per cent. was soluble, and gave on analysis the figures under VI, the insoluble portion having the composition VII. VIII is an analysis of the phonolite of Staufen; sp. gr. 2·452; 62·79 per cent. being insoluble. IX is an analysis of the phonolite of Schwintel; sp. gr. 2·471; 51·87 per cent. being insoluble. X is an analysis of the phonolite of Mägdeberg; sp. gr. 2·4999, with 66·22 per cent. of insoluble constituents.

In the phonolite tuffs of Hegau, the author found brown, glassy, rounded nodules resembling volcanic bombs; sp. gr. 2·221. An analysis gave the figures under XI:—

	I.	II.	III.	IV.	V.	VI.
SiO <sub>2</sub> .....	55·01	47·69	47·68	45·07	51·02	32·61
Al <sub>2</sub> O <sub>3</sub> .....	21·67	25·65	25·24	8·80	18·63	23·76
TiO <sub>2</sub> .....	0·27	—	—	—	trace	—
Cu.....	0·12	0·18	trace	0·71	0·15	—
Mn.....	0·22	0·056	trace	3·07	0·59	0·28
Fe <sub>2</sub> O <sub>3</sub> .....	1·95	1·86	2·24	8·13	3·14	0·98
FeO.....	1·86	—	—	22·65	0·84	1·09
CaO.....	2·12	0·64	0·55	0·81	7·89	15·03
MgO.....	0·13	—	—	2·98	1·02	1·19
Na <sub>2</sub> O.....	9·78	14·76	14·35	4·28	4·13	6·47
K <sub>2</sub> O.....	3·54	—	—	3·68	6·08	2·97
Cl.....	0·08	—	—	—	0·09	0·23
SO <sub>3</sub> .....	0·41	0·89	0·71	—	0·29	0·74
P <sub>2</sub> O <sub>5</sub> .....	0·08	—	—	—	0·16	0·41
H <sub>2</sub> O.....	2·17	8·82	9·45	—	1·10	2·81
Organic matter.....	—	trace	trace	—	4·53	11·56
Total.....	99·41	100·54	100·22	99·18	99·66	100·13

	VII.	VIII.	IX.	X.	XI.
SiO <sub>2</sub> .....	62·88	55·92	55·91	56·43	73·45
Al <sub>2</sub> O <sub>3</sub> .....	15·33	20·35	19·73	20·58	10·11
TiO <sub>2</sub> .....	—	trace	trace	trace	—
Cu.....	—	0·18	—	—	—
Mn.....	0·79	0·50	0·46	0·66	0·40
Fe <sub>2</sub> O <sub>3</sub> .....	4·53	2·16	2·73	2·88	1·05
FeO.....	0·67	0·94	1·36	1·28	0·96
CaO.....	3·26	2·21	2·39	1·45	2·47
MgO.....	0·90	0·62	0·75	0·28	0·06
Na <sub>2</sub> O.....	2·63	8·35	7·24	8·62	3·94
K <sub>2</sub> O.....	8·12	4·83	2·13	4·23	0·79
Cl.....	—	0·06	0·10	0·07	0·56
SO <sub>3</sub> .....	—	0·23	0·21	0·22	1·24
P <sub>2</sub> O <sub>5</sub> .....	—	0·18	0·18	0·06	—
H <sub>2</sub> O.....	—	3·51	4·33	2·90	5·35
Organic matter.....	—	—	1·89	—	—
Total.....	99·11	100·04	99·41	99·66	100·38

B. H. B.

**Action of Water containing Carbonic Acid on the Trachyte of Gleichenberg.** By C. CLAR (*Jahrb. f. Min.*, 1884, 1, Ref., 229).—100 grams of finely powdered trachyte from the quarry near the Klausner spring at Gleichenberg, together with 2 litres of distilled water saturated with CO<sub>2</sub> at a pressure of 10 atmospheres, were rotated for seven weeks in a tinned copper cylindrical vessel. The analysis of the clear fluid gave for 2000 c.c. the figures under II; I gives the results of the analysis of the rock; III, the composition

of the fluid per litre; and IV, that of the Klausner spring also per litre.

	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.
I. ....	65·01	2·28	1·18	18·12	3·05	0·87
II. ....	0·1291	—	0·0887	—	0·2871	0·0116

	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I. ....	3·38	4·96	1·56	100·41
II. ....	0·0283	0·0338	—	0·8756 gram

	SiO <sub>2</sub> .	FeCO <sub>3</sub> .	MgCO <sub>3</sub> .	CaCO <sub>3</sub> .	K <sub>2</sub> CO <sub>3</sub> .	Na <sub>2</sub> CO <sub>3</sub> .	NaCl.
III. 0·0645	0·0715	0·0149	0·2564	0·0304	0·0301	—	—
IV. 0·7127	0·01037	0·00590	0·02357	—	—	—	0·00025

	Na <sub>2</sub> SO <sub>4</sub> .	K <sub>2</sub> SO <sub>4</sub> .	Na <sub>3</sub> PO <sub>4</sub> .	Al <sub>2</sub> P <sub>2</sub> O <sub>5</sub> .	Total.
III. —	—	—	—	—	0·4678
IV. 0·01263	0·00695	0·00125	0·00098	0·13317	—

B. H. B.

**Tachylyte of the Western Isles of Scotland.** By J. W. JUDD and G. A. J. COLE (*Journ. Geol. Soc.*, **39**, 444—464; and *Jahrb. f. Min.*, 1884, **1**, Ref., 236—237).—Basalt-glass or tachylyte has been detected, by the authors, in five places only, viz.: Lamlash, near Arran; the Beal, near Portree, in Skye; Sorne, in Mull; between Gribun and Kilfinichen, in Mull; and Screpidale, in Raasay.

Tachylyte is always found in the Hebrides as a selvage to dykes, and some varieties differ from any tachylyte hitherto described by their high sp. gr. (2·9), and by their low percentage of SiO<sub>2</sub> (45).

From a consideration of the chemical composition of tachylytes, the authors come to the conclusion that the basalts which show a tendency to the vitreous condition are those with a high percentage of silica and alkalis. This is confirmed by the composition of the basalt-glass of the Beal, which was found to be—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	CaO.	MgO.	Na <sub>2</sub> O <sub>3</sub> .	K <sub>2</sub> O.	Ignition.	Total.
52·59	17·33	11·14	0·66	6·47	2·62	4·24	2·40	3·27	100·72

The basic glasses of Sorne, Screpidale, and Gribun form much narrower selvages than the more acid ones of the Beal and Lamlash. In its microscopic characters, basalt-glass was found to resemble other vitreous rocks. In the gradual transition into basalt, all stages of devitrification can be observed.

B. H. B.

## Organic Chemistry.

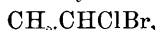
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**Haloïd Derivatives of Ethane.** By L. HENRY (*Compt. rend.*, 97, 1491—1494).—Monochlorethylene dibromide,  $\text{CH}_2\text{Br}.\text{CHClBr}$ , when treated with alcoholic potash in molecular proportions, yields pure potassium bromide, and unsymmetrical chlorobromomethylene,  $\text{CH}_2:\text{CClBr}$ , boiling at  $62-63^\circ$ . The bromine in the chain  $\text{CH}_2\text{Br}$  is alone eliminated. Potassium cyanide produces the same result.

Monobromomethylene dibromide,  $\text{CH}_2\text{Br}.\text{CHBr}_2$ , when treated with potash, sodium ethylate, potassium acetate, &c., in alcoholic solution, yields unsymmetrical dibromomethylene,  $\text{CH}_2:\text{CBr}_2$ , boiling at  $86-88^\circ$ . The bromine eliminated is exclusively that in the chain  $\text{CH}_2\text{Br}$ .

When 2 mols. monochlorethylene dibromide are gently heated with 1 mol. antimonic chloride, dichloromonobromethane,  $\text{CH}_2\text{Br}.\text{CHCl}_2$ , boiling at  $137-138^\circ$ , is obtained, and this, when treated with alcoholic potash, yields unsymmetrical dichlorethylene,  $\text{CH}_2:\text{CCl}_2$ , boiling at  $35-37^\circ$ . The bromine in the chain  $\text{CHClBr}$  is alone attacked by the antimonic chloride.

Ethylidene bromide reacts with antimonic chloride more energetically than does ethylene bromide, and yields exclusively ethylidene chloride boiling at  $59^\circ$ , without any intermediate formation of



even when the substances are in the proportion of 1 mol. antimonic chloride to 2 mols. ethylidene bromide. In the case of ethylene bromide, the bromine is replaced successively with formation of



and finally  $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ . This difference in the mode of action of the two isomerides illustrates the difference which exists between a *monatomic multiple compound*, such as  $\text{CH}_2\text{Br}.\text{CH}_2\text{Br}$ , and a *polyatomic monocarbon compound*, such as  $\text{MeCHBr}_2$ .

When monobromomethylene bromide is treated with antimonic chloride (not in excess), dichloromonobromethane,  $\text{CH}_2\text{Br}.\text{CHCl}_2$ , boiling at  $137-138^\circ$ , is exclusively obtained even when the proportions are 1 mol.  $\text{SbCl}_5$  and 2 mols.  $\text{C}_2\text{H}_3\text{Br}_3$ ; and this when treated with alcoholic potash yields unsymmetrical dichlorethylene,  $\text{CH}_2:\text{CCl}_2$ , boiling at  $35-37^\circ$ .

These different reactions of the chains  $\text{CH}_2\text{Br}$ ,  $\text{CHBr}_2$ , and  $\text{CHClBr}$  show that with respect to positive reagents the reaction aptitude of bromine is diminished by a diminution in the number of adjoining hydrogen-atoms, or by the replacement of one of them by a negative radicle such as chlorine or bromine; whilst with respect to the negative reagent, antimonic chloride, it is increased under the same conditions.

C. H. B.

**Preparation of Higher Olefines, Dodecylene, Tetradecylene, Cetene or Hexadecylene, and Octadecylene.** By F. KRAFFT (*Ber.*, 16, 3018—3024).—By the action of phosphorus pentachloride

on palmitic acid on the water-bath, and subsequent separation of the phosphorus oxychloride formed, by distillation under reduced pressure, an oil, palmityl chloride,  $C_{16}H_{31}OCl$ , is obtained. This latter acts on normal primary dodecyl alcohol (Abstr., 1883, 1075) with evolution of hydrochloric acid. To complete the reaction the mixture is heated at  $170^{\circ}$ . If molecular quantities are taken, and the product purified by boiling with alcohol, pure dodecyl palmitate,  $(C_{28}H_{56}O_2)$ , is obtained. It is soluble in alcohol, more easily in ether, and crystallises in plates melting at  $41^{\circ}$ . It distils without decomposition at very reduced pressures, but at ordinary atmospheric pressure, or better at 600 mm., it is almost completely decomposed into the fatty acid and the olefine  $C_{12}H_{24}$ . The latter distils at  $96^{\circ}$  by 15 mm. pressure, whilst the palmitic acid distils at  $215^{\circ}$ . This process is that of Smith (*Ann. Chim. Phys.* [3], 6, 40) for the preparation of cetene from spermaceti, modified chiefly as regards the pressure.

In precisely similar way, tetradecyl alcohol, cetyl or hexadecyl alcohol, and octadecyl alcohol form with palmityl chloride, palmitates and hydrochloric acid, and by distillation at reduced pressures these palmitates yield respectively the olefines, tetradecylene, cetene or hexadecylene and octadecylene. Hexadecylene was also prepared from spermaceti (cetyl palmitate), and found identical in physical properties to that obtained from artificially prepared hexadecyl palmitate. The following table gives the physical properties of these olefines:—

		Melting point.	Sp. gr. at the melting point.	Boiling at 15 mm.
Dodecylene . . .	$C_{12}H_{24}$	$-31^{\circ}$	$d_{-31} = 0.7954$	$96^{\circ}$
Tetradecylene ..	$C_{14}H_{28}$	$-12$	$d_{-12} = 0.7936$	$127^{\circ}$
Hexadecylene ..	$C_{16}H_{32}$	$+4$	$d_4 = 0.7917$	$155^{\circ}$
Octadecylene . . .	$C_{18}H_{36}$	$+18$	$d_{18} = 0.7910$	$179^{\circ}$

A. B.

**Action of Acetylene Hydrocarbons on Mercuric Salts.** By KOTCHEROFF (*Bull. Soc. Chim.*, 39, 595—596).—On agitating aqueous solutions of mercuric salts with allylene, white crystalline precipitates are obtained of general formula  $mHgX_2 \cdot nHgO \cdot p(C_3H_4HgO)$ , the values of the coefficients  $m$ ,  $n$ , and  $p$  varying with the mercuric salt used. These precipitates are insoluble in water, but dissolve in acids with formation of acetone. This property, together with their inaptitude to detonate by percussion or rise of temperature, distinguishes them from the precipitates produced by the action of allylene on ammoniacal solutions of silver or copper. The author considers these compounds to be combinations of basic salts of mercury with acetone in which two atoms of hydrogen are replaced by one of mercury. The hydration of acetylene hydrocarbons by means of mercuric salts can be explained by these facts; the reaction is effected in two phases: 1st, an intermediate substance is formed by the combination of a basic salt of mercury with the group  $C_nH_{2n-2}HgO$ ; 2nd, this substance is decomposed by the acid disengaged in the first change, and the basic is converted into a neutral mercuric salt; while the group  $C_nH_{2n-2}HgO$  furnishes an acetone and a neutral salt of mercury



resulting from the interchange of one atom of hydrogen for one of mercury.  
V. H. V.

**Ferric Ethylate and Colloidal Ferric Hydrate.** By E. GRIMAUX (*Compt. rend.*, 98, 105—107).—When 1 mol. of ferric chloride in alcoholic solution is mixed with 6 mols. of sodium ethylate, sodium chloride is precipitated and a deep red-brown limpid liquid is obtained, which is free from chlorine, but contains all the iron in solution as ferric ethylate. The alcohol can be distilled off, and the ferric ethylate is left as a black pasty mass, soluble in absolute alcohol, benzene, chloroform, ether, petroleum, and methyl alcohol. If, however, this residue is heated in a vacuum so as to expel the last traces of the solvent, the small quantity of water present almost completely decomposes the ethylate, and ferric hydroxide separates out. If the operations of filtration, &c., have been conducted in dry air, the ethylate is not completely decomposed. An alcoholic solution of ferric ethylate is not precipitated by a current of dry ammonia, but with dry carbonic anhydride it yields a brown precipitate. Dry hydrogen sulphide reduces it to a ferrous salt, and potassium ferrocyanide precipitates ferric hydroxide.

The action of water varies with the proportion in which it is present. If the alcoholic solution is exposed to a moist atmosphere, or is mixed with a small quantity of water, ferric hydrate is deposited as a jelly. If, however, the alcoholic solution of ferric ethylate is poured into an excess of water, limpid liquids are obtained which have the properties of the solutions of colloidal ferric hydroxide described by Graham. They coagulate spontaneously after some time, and are coagulated by addition of various substances, such as carbonic anhydride, sulphuric acid, tartaric acid, potassium chloride, sodium chloride, river water, &c. Acetic, nitric, and hydrochloric acids and ammonia have no effect. Hydrogen sulphide produces a black precipitate. The time which elapses before coagulation takes place increases with the dilution of the solution, and is diminished by an increase of temperature. A higher temperature is required to produce coagulation the greater the amount of water present, and a solution of 1 vol. ferric ethylate solution in 15 vols. of water is not coagulated even after four hours' ebullition.

The coagulated ferric hydroxide forms a thick jelly, which always fills the vessel even if the solution is dilute. At first it is transparent, but it gradually contracts with elimination of water. The coagulation of the ferric hydroxide varies with the conditions in the same way as the coagulation of blood, a fact which indicates that inorganic colloids are analogous to the nitrogenous colloids of the animal organism.  
C. H. B.

**New Derivatives from Mannitol.** By A. FAUCONNIER and others (*Bied. Centr.*, 1883, 789).—By dry distillation of mannitol, a yellowish-brown liquid was obtained, from which voluminous crystals of the second anhydride of mannitol separated. They were found to agree with the formula  $C_6H_{10}O_4$ ; they melt at  $87^\circ$ , and boil in a vacuum at  $176^\circ$ . With acetic anhydride, a diaceto-compound is

obtained. Phosphorous chloride gives other derivatives, and an ethyl compound is formed when it is heated with ethyl iodide and potash.

J. K. C.

**Influence of the Quantity of the Constituents of Fehling's Solution on the Rate of Separation of Cuprous Oxide by Invert-sugar.** By F. URECH (*Ber.*, 16, 2825—2827).—The author previously described the effect of an excess of invert-sugar (*Abstr.*, 1883, 385), and he now shows that the results obtained are in accordance with theory. With an excess of the constituents of Fehling's solution, the rapidity of separation of cuprous oxide is likewise accelerated provided the amount of water be not increased. With the addition of water the rapidity is diminished; whilst with increased concentration the rate of separation is accelerated to a certain point, beyond which, it gradually becomes diminished. Experiments, in which the quantity of alkali and Rochelle salt was diminished, showed a lower rate of separation. On employing an excess of copper sulphate alone, it is found that the rate of separation is not increased to the same extent as by the employment of an excess of invert-sugar.

A. K. M.

**Action of Sodium-amalgam on Glucoses and Saccharin.**

By C. SCHEIBLER (*Ber.*, 16, 3010—3011).—The quantity of mannitol obtained by the action of sodium-amalgam on a solution of dextrose or levulose is very small, for from 500 grams Krusemann only obtained 40 grams mannitol in each case. This the author considers to be due to the fact that glucose is very unstable in presence of caustic soda, and that as soon as the latter is formed by the action of the sodium-amalgam, a complicated, and as yet unknown, decomposition of the glucose takes place. He considers also that the formation of mannitol may be due to the addition of hydrogen to one of these products of decomposition. In this preliminary notice he states that he undertakes the study of the decomposition of glucoses by alkalis and alkaline earths, and also of the action of sodium-amalgam on saccharin (which is not accompanied with evolution of hydrogen) and on iso-saccharin.

A. B.

**Starch.** By F. MUSCULUS (*J. pr. Chem.* [2], 28, 496—504).—This is a paper written to criticise Salomon's paper (this vol., p. 36) entitled: "The behaviour of starch in the presence of inorganic and organic acids." The author states that Salomon only treats of crystalline soluble starch in his treatise, completely ignoring the amorphous variety. The author himself was the first to prepare crystalline starch. Nägeli obtained amyllum four years later in fine needles, and gave to it the name of amyloextrin. Dilute solutions of crystalline soluble starch give a red coloration with iodine, concentrated solutions yielding a blue colour. The crystalline variety dialyses slowly, and reduces Fehling's solution on boiling. The author suggests that Salomon's solution, with which he tried to reduce alkaline copper solution, was probably too dilute. The amorphous modification is soluble in cold water, and always gives a blue coloration with iodine. It cannot be dialysed, nor does it reduce Fehling's solution. Salomon states that only one dextrin exists, and that the different colours

which it yields with iodine are due merely to admixed soluble starch, and also that the various rotatory and reducing powers are due to the presence of sugar. The author claims that he has previously shown that crystalline soluble starch owes its power of producing a red colour with iodine to the presence of dextrin. Brücke's erythrodextrin consists of dextrin which gives no colour with iodine. The author states that the evidence of the existence of several dextrins does not rest alone on their behaviour with iodine. Bondonneau prepared in 1875 two dextrins which gave no coloration with iodine, but which differed in their solubilities in alcohol and their rotatory powers. The author (*Bull. Soc. Chim.*, 30, 4, 1878) has prepared three dextrins, which gave no iodine coloration, and which differed from one another in their behaviour with diatase. They also differ in the time required to dialyse.

Salomon states that maltose has never been prepared by boiling starch with dilute sulphuric acid: the author (*Zeitschr. f. Physiol. Chem.*, 1879), Dubrunfant, and O'Sullivan have all prepared it in this way. Salomon has fallen into error by assuming that dextrin has a greater rotatory power in an acid solution than in a neutral one; for he has endeavoured to detect the formation of maltose by the variation in the rotatory power of the solution.

J. I. W.

**Contribution to the more exact Knowledge of the Chemical Nature of Starch-grains.** By B. BRUKNER (*Monatsh. Chem.*, 4, 889—912).—In 1856, Nägeli extracted a substance turned blue by iodine, and termed "granulose," from starch-grains, without, however, destroying their form. In 1859 Jessen found that on rubbing starch-grains with water, that a portion of the soluble starch was dissolved. Nasse, in 1866, gave the name amidulin to a soluble body obtained from starch-paste. Nägeli, in 1874, extracted by dilute hydrochloric acid a body essentially different from starch, which he called amylo-dextrin. The first object of the author is to determine the relation existing between these four bodies.

*Amidulin.*—Starch has generally been considered as insoluble in water. Jessen and Delff, by rubbing starch with water, extracted a portion; this might, however, have been due to the conversion into starch-paste by the heat evolved in the crushing of the granules. W. Nägeli imbedded starch-grains, and then cut sections; the portions of the granules were turned blue by iodine, as also was, to some extent, the small quantity of water employed, and hence a portion must have gone into solution. By rubbing dry starch granules, they may be broken, and if subsequently treated by water and filtered, they give a clear solution turned blue by iodine. But on allowing wheaten starch to digest with water for three weeks, filtering, evaporating to one-fifth, and testing with iodine, no blue coloration was obtained; hence it is impossible to extract the inner and soluble starch with water until the outer membrane is either changed or broken; the character of the solution is that of a micellar solution; it is not capable of diffusion. The substance soluble in cold water and coloured blue by iodine, the amidulin of Nasse and the granulose of Nägeli, are identical.

*Starch-paste.*—Schimper and Nägeli are not agreed as to the distinction between swollen starch and starch-paste. Between these two states there is no sharp distinction; thus at 46° potato-starch swells distinctly; at 59° it begins to lose its form; and at 62·5° it is converted into a paste, and shows no trace of the original form. After discussing Nägeli's micellar theory, viz., that the smallest particles of starch and similar substances consist not of molecules, but of larger groups, i.e., micellæ, which owing to their comparatively slow movements, due to their greater size and weight, easily unite into micellar clusters, the author concludes that swollen starch and starch-paste differ in nothing but the aggregate condition of their micellæ; they differ therefore physically but not chemically, and accordingly starch-paste, amidulin, and granulose are identical.

*Erythrogranulose.*—Erythrogranulose and erythrodextrin are the names given to two bodies coloured red by iodine (Brücke). By digesting starch solution with diastase, and testing portions from time to time with iodine and with tannin solution, it was shown that so long as iodine produced a blue coloration, tannin produced a precipitate, but with a red coloration no precipitate was formed, nor under these conditions was a precipitate produced by adding hydrochloric acid: hence the red coloration is due to the presence of dextrin. If very dilute iodine be added to starch-granules (or paste) a red colour is first produced; this is due to the presence of dextrin (erythrodextrin) and its greater solubility in water.

*Amylodextrin.*—W. Nägeli states that soluble starch is distinguished from amylodextrin by being precipitated from solution by tannin and by lead acetate, and further that freshly precipitated starch is insoluble in water, whilst freshly precipitated amylodextrin is soluble. None of these differences can be confirmed. Further, amylodextrin does not, like starch, swell up with an alkaline solution, but simply dissolves; this, however, is not a distinctive test, since precipitated starch behaves exactly like amylodextrin; amylodextrin is tinted by organic matter just as starch is. It is also stated that Trommer's copper test is not reduced by amidulin, but is by amylodextrin; but it has been shown that the starch-grains themselves contain dextrin, and further, during the progress of the test, the starch becomes converted into dextrin and into sugars, and, still more important, dextrin is formed during the preparation of amylodextrin.

The author has been quite unable to confirm the statement as to the crystalline nature of amylodextrin. Amidulin and amylodextrin are identical. That amyduin—a body not capable of diffusion, can be extracted from starch-grains by dilute acid, is explained by the action of the acid on the micellar aggregates.

*The Iodine Reaction.*—The so-called iodide of starch is no chemical compound; it has been stated to be decomposed when heated; this depends on the affinity of warm water for iodine being greater than that of cold water; and if this greater absorptive power be satisfied by addition of more iodine, then the blue colour is not destroyed even by boiling. The author considers the blue colour to be simply due to the solution of iodine in potato-starch, just as violet and brown colours are obtained on solution in chloroform and water respectively.

Potato- and arum-starch yield blue colorations, wheat- and rice-starch yield violet, but after boiling they also are turned blue by iodine. Starch-grains have a greater attraction for iodine than unorganised starch; thus a cold clear solution prepared from crushed starch-grains and coloured blue by iodine, is completely decolorised by adding whole starch-grains. Similarly, it is shown that starch grains attract iodine more energetically than dextrin, the red solution being decolorised, and the starch-grains turning blue.

In conclusion, soluble starch, starch-paste, granulose, amidulin, and amylopectin are identical, *i.e.*, give identical reactions, as also are erythrogranulose, erythropectin, and dextrin. H. B.

**Action of Cuprammonium Solutions of Cellulose on Polarised Light.** By A. LEVALLOIS (*Compt. rend.*, **98**, 44).—Solutions of cotton, flax, Berzelius' paper, and German filter-paper in Schweitzer's reagent were examined with polarised light by means of the electric arc. All the solutions are strongly lævogyrate, and the degree of rotation seems to be proportional within certain limits to the concentration of the solution. This fact would indicate that the ammonio-cupric compound of cellulose is not definite. It is observed, however, that the intensity of the blue colour diminishes when the liquid is highly charged with cellulose. C. H. B.

**Action of Ammonia Gas on Methyl Nitrate.** By E. DUVILLIER and H. MALBOT (*Compt. rend.*, **97**, 1487—1488).—When ammonia gas is passed into methyl nitrate mixed with about one-tenth its volume of wood-spirit, and contained in a flask connected with an inverted condenser, the ammonia is absorbed with development of heat, and when the liquid is saturated it contains different ammonias in approximately the following proportions:—

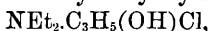
Ordinary ammonia .....	5
Tetramethylammonium oxide .....	3
Monomethylamine .....	2
Dimethylamine and trimethylamine .....	Very small quantities

Under these conditions, tetramethylammonium oxide and not monomethylamine is the principal product (compare Duvillier and Buisine, *Abstr.*, 1880, 545). C. H. B.

**Trimethylamine Aurochloride.** By O. HESSE (*Ber.*, **16**, 3014).—The author states that in 1857 (*J. pr. Chem.*, [2], **27**, 425) he determined the formula and described the properties of this compound lately communicated by Zay (*Abstr.*, 1884, 286). A. B.

**Oxallyldiethylamine.** By E. REBOUL (*Compt. rend.*, **97**, 1556—1558).—Oxallyldiethylamine,  $\text{NEt}_2\text{C}_3\text{H}_6\text{O}$ , is the most volatile of the bases obtained by the action of epichlorhydrin on diethylamine. (See next Abstract.) It is a thick colourless liquid with a powerful poisonous odour resembling that of diethylamine. It boils at about  $160^\circ$ , gradually becomes yellow when exposed to light, and is very

soluble in water. When treated with excess of dilute hydrochloric acid and then with platinum tetrachloride, it yields garnet-red rhombic prisms which are not oxallyldiethylamine platinochloride, but are the platinochloride of a base, chlorhydroxyallyldiethylamine,

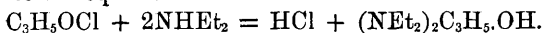


formed by the union of HCl with the unsaturated radicle oxallyl,  $\text{C}_3\text{H}_5\text{O}$ .

This chlorhydroxyallyldiethylamine is the first product of the action of epichlorhydrin on diethylamine. The epichlorhydrin behaves like chloropropylene oxide, and unites directly with 1 mol. diethylamine after the manner of the glycollic anhydrides,  $\text{C}_3\text{H}_5\text{OCl} + \text{NHEt}_2 = \text{NEt}_2 \cdot \text{C}_3\text{H}_5(\text{OH})\text{Cl}$ , and this product reacts with a second molecule of diethylamine with formation of hydroxyallyltetraethylamine and liberation of hydrochloric acid,  $\text{NEt}_2 \cdot \text{C}_3\text{H}_5(\text{OH})\text{Cl} + \text{NHEt}_2 = \text{HCl} + (\text{NEt}_2)_2\text{C}_3\text{H}_5\text{OH}$ .

C. H. B.

**Hydroxyallyldiamines.** By E. REBOUL (*Compt. rend.*, **97**, 1488—1491).—Epichlorhydrin and diethylamine react at the ordinary temperature, with gradual development of heat; and unless the mixture is cooled, the temperature rises sufficiently high to cause an explosion even in a strong, sealed flask. The product of the reaction is sometimes a very thick syrupy liquid, sometimes is mainly solid, and contains several bases in proportions depending on the temperature and on the proportions of the original substances. It is made alkaline with potash, and the free bases are distilled off, or better, are extracted with ether. The chief products are a monamine, diamine, and triamine, together with polyamines. With 1 vol. epichlorhydrin and 1.5 vol. of diethylamine, the principal product is the diamine formed according to the equation—



This equation simply represents the final products. The diamine is really formed by the action of the diethylamine on a chloro-monamine formed by the union of 1 mol. epichlorhydrin with 1 mol. diethylamine. This diamine,  $(\text{NEt}_2)_2\text{C}_3\text{H}_5\text{OH}$ , is *hydroxyallyltetraethylamine*. It is a very stable liquid lighter than and only slightly soluble in water; it boils at 236—238° without decomposition under atmospheric pressure. It forms a crystalline orange platinochloride,



and with sulphuric and oxalic acids it forms neutral syrupy salts which do not crystallise.

In a sealed tube at 100° hydroxyallyltetraethylamine combines with 2 mols. ethyl iodide, forming a syrupy liquid which solidifies to a translucent mass. This product could not be obtained in crystals, but it is *hydroxyallylhexethylammonium iodide*,  $\text{N}_2\text{Et}_6\text{C}_3\text{H}_5\text{OH}\text{I}_2$ .

The diamine mixes perfectly with allyl bromide in the cold, and after some time the liquid becomes turbid, and a syrupy upper layer consisting of a compound of 2 mols. allyl bromide with 1 mol. hydroxyallyltetraethylamine separates out. The diamine also combines directly in the cold with ethylene bromide in the proportion of equal molecules.

Epichlorhydrin reacts violently with ethylamine, forming hydroxy-

allyldiethyldiamine,  $(\text{NHEt})_2\text{C}_3\text{H}_5\text{OH}$ , a colourless syrup which dissolves in water in all proportions, and boils at about  $185^\circ$  without decomposition.

C. H. B.

**Action of Heat on Aldol and Paralldol.** By A. WURTZ (*Compt. rend.*, **97**, 1525—1530).—The principal products of the action of heat on aldol are crotonaldehyde and water, but the exact nature of the decomposition depends on the temperature and on the purity of the original substance. When the aldol contains small quantities of crotonaldehyde and gives a slight turbidity with water, the product of decomposition consists of a small colourless and aqueous lower layer and an abundant dark-brown or black upper layer which consists mainly of crotonaldehyde together with condensation-products of high boiling point. Purer specimens of aldol, on the other hand, when heated in sealed tubes at  $160^\circ$  or  $170^\circ$  for four or six hours, yield a homogeneous almost colourless product which contains a smaller proportion of crotonaldehyde than in the first case, together with products boiling between  $250^\circ$  and  $300^\circ$ . This higher fraction contains a substance which is soluble in water, and the yield of which is never more than 15 per cent. under the most favourable conditions. Very often it is not formed at all, and the conditions under which its formation takes place could not be definitely ascertained. It can, however, be obtained in larger proportion by heating paralldol in sealed tubes at  $170^\circ$  for about four hours. The almost colourless product is distilled, and the fraction boiling between  $260^\circ$  and  $300^\circ$  is washed with water, treated repeatedly with small quantities of ether to remove oily products, the solution concentrated in a vacuum to a syrupy consistency, and then distilled in a vacuum. This new compound has the composition  $\text{C}_4\text{H}_8\text{O}_3$ , and is a viscous colourless liquid which boils at about  $170^\circ$  under a pressure of 15 mm., and at about  $280^\circ$  at the ordinary pressure; sp. gr. at  $0^\circ = 1.095$ . Its vapour-density by V. Meyer's method in mercury vapour is about 3.

This compound has the appearance and general characters of a glycol. With nascent hydrogen, it yields  $\beta$ -butyl glycol. It reacts energetically with acetic chloride, benzoic chloride, and phosphorus pentachloride with evolution of hydrochloric acid and formation of ethereal derivatives, and when heated with acetic anhydride it yields an acetyl derivative. It does not combine energetically with bromine in the cold, and this would indicate that it does not contain an open chain of 4 carbon-atoms two of which are united by a double bond, a supposition which is also confirmed by its boiling point.

When the substance is heated with an excess of acetic anhydride, first at  $100^\circ$  and finally at  $110^\circ$ , it yields a colourless liquid which boils at  $176^\circ$  under a pressure of 15 mm., and at about  $275^\circ$  under ordinary pressure; sp. gr. at  $0^\circ = 1.095$ . It is insoluble in water, and is saponified when heated with this liquid in sealed tubes for several days. The only formula which agrees with the percentage composition of this compound and with the amount of acid which it yields on saponification, is that of a diacetyl derivative of butyl glycol oxybutyrate,



It would appear to be a compound ether containing two hydroxyls, and therefore possessing some of the properties of glycols. When saponified it yields butyl glycol, acetic acid, and  $\beta$ -oxybutyric acid or its derivative crotonic acid. This supposition does not agree with the vapour-density of the substance or of its acetyl derivative, but the determinations were not satisfactory.

C. H. B.

**Pentachloracetone.** By C. CLOËZ (*Bull. Soc. Chim.* [2], **39**, 636—641).—Pentachloracetone is generally prepared by the action of hydrochloric acid and potassium chlorate on quinic or citric acid, but the process presents the difficulty of the incomplete removal of chlorine oxides from the final product. In this paper it is proposed to prepare this substance either by passing chlorine through a tubulure, filled with pumice stone, over which trickles a continuous stream of citric acid solution; the whole apparatus being kept at a temperature of  $100^{\circ}$ : or secondly, by the action of dry chlorine on dry acetone in presence of sunlight. Thus prepared, pentachloracetone is a mobile liquid boiling at  $192^{\circ}$ , of sp. gr. = 1.576, and transformed by ammonia into dichloracetamide and chloroform.

But by the action of chlorine on symmetrical dichloracetone, there is produced an isomeride of pentachloracetone boiling at  $185^{\circ}$ , sp. gr. = 1.617, and converted by ammonia into trichloracetamide without a trace of chloroform. According to prevalent views, the molecule of acetone is represented by a formula in which the two methyl-groups are symmetrically associated with the carbonyl-group; if these views be correct, then only one pentachloracetone is possible. On the other hand, if the hypothesis of Chancel and Gerhardt be correct, that one methyl-group is less intimately associated with the carbonyl-group than the other, then one pentachloracetone might be represented by the formula  $C_2HCl_2O.CCl_3$ , converted into dichloracetamide and chloroform, the other by the formula  $C_2Cl_3O.CHCl_2$ , converted into trichloracetamide.

V. H. V.

**Duplothiacetone.** By W. SPRING (*Bull. Soc. Chim.*, **40**, 66—71).—By the action of phosphorus pentasulphide on acetone, Wislicenus obtained a thiacetone,  $2C_3H_6S$ , boiling between  $183^{\circ}$  and  $185^{\circ}$ , which, according to Claus and Kühlze, can be obtained from isopropyl mercaptan, and is transformable into isopropylsulphonic acid. On distilling the crude product of the above reaction, the author obtained besides methyl and isopropyl mercaptans, a liquid of no fixed boiling point, which decomposed continuously into duplothiacetone and acetone; this substance, probably of formula  $C_3H_6S.C_3H_6O$ , may be called oxythiacetone.

By sodium-amalgam, duplothiacetone is transformed into isopropyl mercaptan, and a substance,  $C_6H_{20}S'$ , the sulphur analogue of mesityl oxide. With nitric acid, duplothiacetone yields besides other oxidation products, isopropyl- and methyl-sulphonic acids, and a nitroso-acid,  $C_9H_{10}(SO_3H)(NO)_2$ , probably derivable from the hitherto unknown thiophorone,  $C_9H_{14}S$ .

Chlorine converts duplothiacetone into isopropylsulphonic acid and



sulphonyl chloride and chlorine derivatives of formulæ,  $C_6H_5SClO$ , and  $C_6H_5SCl_2O$ , probably also referable to mesityl sulphide.

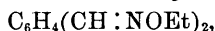
V. H. V.

**Isonitroso-compounds.** By B. WESTENBERGER (*Ber.*, 16, 2991—2998).—*Isonitrosoisopropylacetone*,  $Me.CO.C(NO.H).CHMe_2$ . This member of the series of isonitrosoketones, of which nitrosoacetone is the first, is obtained by dissolving isopropyl acetoacetate in dilute potash, treating the solution with sodium nitrite in excess, and afterwards acidifying it. On evaporating the ethereal extract, it yields white crystals melting at  $75^\circ$ , and soluble in alcohol, ether, alkalis, and hot water, but only sparingly soluble in cold water.

*Enanthaldoxime*,  $C_7H_{13}NO$ .—This aldoxime is obtained by the action of hydroxylamine on an alcoholic solution of enanthaldehyde. It crystallises from alcohol in white plates melting at  $50^\circ$  and boiling at  $125^\circ$ , and is soluble in ether and hot water. Unlike the known aldoximes, it does not combine with dry hydrochloric acid or with sodium ethylate to form a sodium compound, but with silver nitrate it yields a compound,  $(C_7H_5NO)_2.AgNO_3$ ; this is soluble in hot water, and was proved to be a nitrite by its reaction with diphenylamine. *Ethyl enanthaldoxime*,  $C_9H_{19}NO$ , formed by the action of sodium ethylate and ethyl iodide, is an oil boiling at  $185$ — $187^\circ$ .

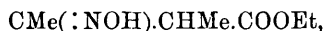
*Anisaldoxime*,  $C_8H_9O_2N$ , melting at  $45^\circ$ , and *Cuminaldoxime*,  $C_{10}H_{13}NO$ , melting at  $52^\circ$ , obtained by the action of hydroxylamine on anisylaldehyde and cuminaldehyde respectively, are also crystalline substances soluble in alcohol and ether.

*Terephthalaldoxime*,  $C_6H_4(CH:NOH)_2$ , obtained by the action of hydroxylamine on terephthaldehyde, is also a crystalline substance melting at  $114^\circ$ , soluble in alcohol and ether. This compound was prepared in order to ascertain if one or both aldehyde-groups would be acted on by hydroxylamine. The *ethyl derivative*,

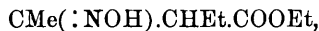


melts at  $55^\circ$ ; an *acetyl derivative*,  $N\bar{Ac}:CH.C_6H_4.CH:N.O\bar{Ac}$ , melting at  $155^\circ$ , was obtained by the action of acetic chloride.

*Action of Hydroxylamine on Ethylic Acetoacetate.*—By this reaction ethylic  $\beta$ -isonitrosobutyrate,  $CMe(:NOH).CH_2.COOEt$ , is formed as an oil which neither crystallises, nor distils without decomposition. By saponifying it with alkali in the cold,  $\beta$ -isonitrosobutyric acid is obtained melting at  $140^\circ$  with decomposition, and but sparingly soluble in water, alcohol, or ether. The following have also been prepared: *Ethylic isonitrosomethylethylacetate*,



from ethylic methylacetoacetate; *ethylic isonitrosodiethylacetate*,



from ethylic ethylacetoacetate; and *ethylic isonitrosotriethylacetate*,  $CMe(:NOH).CET_2.COOEt$ , from ethylic diethylacetoacetate.

A. B.

**Action of Acids on Methyl Acetate.** By W. OSTWALD (*J. pr. Chem.* [2], 28, 449—495).—When aqueous solutions of ethyl acetate,

methyl acetate, or similar compounds are allowed to stand at the ordinary temperature, they undergo a slow decomposition into alcohol and acid. When dilute acids are added, the process of decomposition is accelerated. It is found that the velocity of the action is dependent on the quantity and the nature of the acid which is present. The acid does not take any chemical part in the reaction. According to Guldberg and Waage, if  $a$  be the amount of the acid, and  $b$  the amount of the salt, then the amount  $dx$  decomposed in an interval of time  $dt$ , will be proportional to the product of the masses taking part in the reaction, when  $a$  remains unaltered and  $b$  and  $x$  decrease.

Therefore if  $a$  be a constant, we have  $\frac{dx}{dt} = c \cdot a (b - x)$  or  $-\log (b - x) = cat - \log b$  (the log being natural). This equation  $\log b - \log (b - x) = cat$  represents very correctly the progress of this reaction.  $b$  represents not the whole of the salt which is present; but only that part which is decomposable. The author finds that if acetone be added to the solution, the progress of the decomposition is retarded in exact proportion to the amount of acetone which is present. Methyl alcohol exerts a greater, but not quite so regular, influence. Ethyl alcohol occasions great irregularity in the decomposition, and the general formula does not appear to be trustworthy in this case.

Experiments made with hydrochloric, hydrobromic, and nitric acids, show conclusively that the rate of decomposition varies with the amount of acid present.

The nature of the acid employed affects the rate of decomposition. The following numbers, given in columns I and II, compiled from an extensive series of experiments, represent the velocities for various acids referred to  $\text{HCl} = 100$ . Column III contains results obtained by the volume method (*J. pr. Chem.* [2], 18, 362, 1878). Columns IV and V consist of figures obtained in an investigation of the solubility of calcium oxalate in acids, made for the purpose of estimating their affinities :—

	I.	II.	III.	IV.	V.
Hydrochloric acid .....	100·0	100·0	98·0	97·9	100·0
Hydrobromic „ .....	89·3	99·1	—	99·0	94·9
Hydriodic „ .....	96·3	98·1	—	—	—
Nitric „ .....	91·5	95·7	100·0	100·0	110·0
Chloric „ .....	94·4	97·2	—	99·8	103·6
Sulphuric „ .....	54·66 (109·32)	73·93 (104·56)	66·0	74·2	70·0
Methyl hydrogen sulphate ..	100·74	100·37	—	—	—
Ethyl hydrogen „ ....	98·67	99·33	—	—	—
Propyl hydrogen „ ....	97·96	98·98	—	—	—
Isobutyl hydrogen „ ....	97·06	98·58	—	—	—
Amyl hydrogen „ ....	95·88	97·82	—	—	—
Ethylsulphonic acid .....	97·88	98·94	—	—	—
Isethionic „ .....	97·75	98·87	—	—	—
Eenzenesulphonic „ .....	99·09	99·54	—	—	—
Eormic „ .....	1·310	11·49	3·9	12·90	2·59

	I.	II.	III.	IV.	V.
Acetic acid.....	0·345	5·87	1·23	7·35	1·05
Propionic „.....	0·304	5·51	1·04	—	—
Butyric „.....	0·299	5·47	0·98	—	—
Isobutyric „.....	0·268	5·18	0·92	—	—
Monochloroacetic acid.....	4·30	20·8	7·0	21·3	5·1
Dichloroacetic „.....	23·04	48·0	33·0	48·8	18·3
Trichloroacetic „.....	68·2	82·6	80·0	89·9	64·2
Lactic „.....	0·901	9·49	3·3	13·3	4·1
Oxyisobutyric „.....	0·921	9·60	—	—	—
Trichlorolactic „.....	6·90	26·3	—	—	—
Pyroracemic „.....	6·70	25·9	—	—	—
Oxalic „.....	17·46	43·0	—	—	—
Malonic „.....	2·87	16·9	—	—	—
Succinic „.....	0·496	7·04	1·45	9·30	2·05
Malic „.....	1·181	10·86	2·82	12·05	5·05
Tartaric „.....	2·296	15·15	5·2	14·16?	4·62
Racemic „.....	2·296	15·15	—	—	—
Citric „.....	1·635	12·79	—	14·44	3·06

J. I. W.

**New Method of Preparing Glycocine.** By M. NENCKI (*Ber.*, 16, 2827—2828).—This consists in heating chloroacetic acid with three times its weight of dry powdered ammonium carbonate, the operation being conducted in an open flask in a bath of sulphuric acid. The action begins at 60—70°, and on gradually raising the temperature to 130°, the mass, after previously melting, again solidifies. The melt is dissolved in water, boiled with lead oxide to expel the ammonia, the lead separated by means of hydrogen sulphide, and the filtrate concentrated on a water-bath. The yield by this method is 20 per cent. of theory.

A. K. M.

**Action of Carbamide on Ethylic Acetoacetate.** By R. BEHREND (*Ber.*, 16, 3027—3028).—Carbamide and ethylic acetoacetate combine at 100—110° with separation of water. The product,  $C_7H_{12}N_2O_3$ , is insoluble in water, soluble in ether and alcohol, and forms crystalline needles melting at 147°. The quantity is, however, small, being only 10 to 20 per cent. of the acetoacetate employed. On heating the new compound with dilute acids, it is reconverted into carbamide and ethylic acetoacetate. With sodium acetate, it readily forms a compound of the formula  $C_5H_7N_2O_3Na$ . The author is investigating the constitution and properties of these compounds, and the action of substituted carbamides and ketones on ethylic acetoacetate.

A. B.

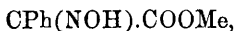
**Preparation of Glycollic Acid.** By A. HÖLZER (*Ber.*, 16, 2954—2957).—On boiling monochloroacetic acid with water, the glycollic acid formed is prevented by the resulting hydrochloric acid from crystallising. In the use of caustic potash a difficulty is found in the separation of the potassium glycollate from potassium chloride; and in the use of caustic lime a diglycollate is obtained along with calcium glycollate, the separation of the two being difficult. The

author's method is to add 560 grams powdered marble to 500 grams monochloroacetic acid, dissolved in 4 litres water, and to heat these in a flask with upright condenser on the water-bath for two or three days. On cooling, a crystalline mass is obtained, which consists of two or three layers; the top one is a hydrated calcium glycolate,  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 + 4\text{H}_2\text{O}$ ; the second, which does not always exist, is anhydrous calcium glycolate; and the lowest is a double salt of calcium chloride and glycolate,  $\text{CaClC}_2\text{H}_3\text{O}_2 + 3\text{H}_2\text{O}$ . The second layer can be converted into the first by dissolving it in boiling water and recrystallising; and the third also by dissolving it in boiling water, recrystallising, and forcing out the more soluble calcium chloride in a filter-press. About 66 per cent. of the theoretical quantity can thus be obtained. The acid is obtained by precipitating the calcium salt with oxalic acid. The author finds that calcium glycolate crystallises with 4 mols. of water of crystallisation, and gradually loses part of them over sulphuric acid. A. B.

**Water of Crystallisation of Normal and Acid Potassium Succinate.** By T. SALZER (*Ber.*, 16, 3025—3027).—Owing to the improbability of these salts having the same number of molecules of water of crystallisation and also to the disagreement in Fehling's and Döppling's determinations, fresh specimens were prepared and analysed. The author finds that normal potassium succinate crystallises over sulphuric acid in large thin plates as  $\text{C}_4\text{H}_4\text{O}_4\text{K}_2 + 3\text{H}_2\text{O}$ , which at  $100^\circ$  lose 2 mols.  $\text{H}_2\text{O}$ ; the third at  $130^\circ$ . The acid salt was found to have the formula  $\text{KHC}_4\text{H}_4\text{O}_4 + 2\text{H}_2\text{O}$ . A. B.

**Action of Hydroxylamine on Carboxytartronic Acid. Ethers of Isonitrosophenylacetic Acid.** By A. MÜLLER (*Ber.*, 16, 2985—2987).—By acting on sodium carboxytartrate with hydroxylamine nitrate and subsequent addition of silver nitrate, a precipitate is obtained. On removing the silver from this precipitate by hydrochloric acid, filtering, and evaporating the solution over sulphuric acid in a vacuum, an acid crystallised out in prisms; on analysis this was found to be di-isonitrososuccinic acid. Its formation is represented by the equation  $\text{COOH.CO.CO.COOH} + 2\text{H}_2\text{N.OH} = 2\text{H}_2\text{O} + \text{COOH.C(N.OH).C(N.OH).COOH}$ . This acid melts at  $128^\circ$ , but explodes at a somewhat higher temperature. It gives insoluble salts with the heavy metals. Some of its properties are similar to those of isonitrosomalonic acid. This formation is in accordance with the constitutional formula  $\text{COOH.CO.CO.COOH}$  for carboxytartronic acid, as advocated by Kekulé (*Abstr.*, 1884, 41), but not with the supposed formula  $\text{C(COOH)}_3\text{OH}$ .

The author has prepared methyl isonitrosophenylacetate,



melting at  $138^\circ$ , from isonitrosophenylacetic acid, and by the action of sodium ethylate and methyl iodide on this, dimethyl isonitrosophenylacetate,  $\text{CPh(NO.Me).COOMe}$ , melting at  $55\text{--}56^\circ$ , is formed. Both compounds are crystalline; the former is soluble in boiling water,

whilst the latter is insoluble, and both decompose on attempting to distil them.

A. B.

**Furfuraldehyde Derivatives.** By E. ODERNHEIMER (*Ber.*, 16, 2988—2991).—This investigation of the action of hydroxylamine on compounds of the furfuraldehyde group was undertaken in the hope of throwing some further light on the constitution of the radical  $C_4H_3O$ .

*Furfuraldoxime*,  $C_4H_3O.CH:NOH$ , is obtained by the action of 2 mols. hydroxylamine hydrochloride and soda on furfuraldehyde, and is deposited in thin, white, odorous refractive crystals from its solution in light petroleum, but in spite of frequent recrystallisations, it had an inconstant melting point. Analysis leads to the above formula. An attempt to replace the second oxygen-atom by the action of hydroxylamine hydrochloride in excess failed, and the author has also failed to obtain an isomeride of the compound, which, owing to the variable melting point, was suspected to be present. *Furfuraldoxime* melts at  $89^\circ$ , and is soluble in ether, alcohol, carbon bisulphide, benzene, and glacial acetic acid, and sparingly in water. It distils at  $201\text{--}208^\circ$  with slight decomposition. By oxidising reagents, it is decomposed with evolution of hydrocyanic acid, but reducing reagents give negative results. It evolves hydroxylamine when boiled with acids.

*Furfuraldoxime hydrochloride*,  $C_4H_3O.CH:NOH.HCl$ , is obtained by the action of dry hydrochloric acid gas on the ethereal solution of furfuraldoxime; it is a white crystalline mass, soluble in alcohol and water, and readily decomposed on exposure to air with evolution of hydrochloric acid. The sodium salt,  $C_4H_3O.CH:NONa + 3H_2O$ , obtained by the action of sodium ethylate on an ethereal solution of furfuraldoxime, is soluble in alcohol, and gives characteristic coloured precipitates with the salts of the heavy metals.

*Ethylfurfuraldoxime*,  $C_4H_3O.CH:NOEt$ , is obtained by the action of sodium ethylate and ethyl iodide on the aldoxime, and extraction with ether. *Furfuraldoxime* yields dye-stuffs with aniline, toluidine, &c.

Hydroxylamine does not act on pyromucic acid or on furfuryl alcohol; it is also without action on phthalanil and phthalimide.

A. B.

**Synthesis of Pyrocoll.** By G. L. CIAMICIAN and P. SILBER (*Gazzetta*, 563—567).—This substance, obtained by the dry distillation of gelatin (*Abstr.*, 1881, 295), and represented by the empirical formula  $C_5H_3NO$ , has been regarded as probably consisting of the anhydride of carbopyrrolic acid,  $C_5H_5NO_2 - H_2O = C_5H_3NO$ ; but it has not hitherto been prepared by dehydration of this acid. Moreover, its vapour-density indicates that its true formula is  $C_{10}H_5N_2O_2$ , and this conclusion is confirmed by the existence of a monobromoderivative,  $C_{10}H_5BrN_2O_2$ . The dehydration of carbopyrrolic acid cannot be effected by means of the ordinary dehydrants,  $P_2O_5$ ,  $SO_4H_2$ , or  $HCl$ , but the authors have effected it through the medium of the acetyl-derivative, which, when heated to  $300^\circ$ , gives off a molecule of acetic acid and leaves pyrocoll,  $2C_5H_4\overline{Ac}NO_2 = 2\overline{Ac}OH + C_{10}H_5N_2O_2$ .

The preparation is effected by distilling a solution of carbopyrrolic acid in acetic anhydride, and heating the oily residue to the temperature above mentioned; the pyrocoll then sublimes in yellow scales, which melt at  $267^{\circ}$ , and exhibits all the properties of pyrocoll obtained from gelatin.

H. W.

**The Thiophene and Pyrroline Groups.** By V. MEYER (*Ber.*, 16, 2968—2975).—In this preliminary notice the field which the author with his collaborators intends to take up in the study of the derivatives and homologues of thiophene is defined. For purposes of nomenclature, it is proposed to call the radical  $C_4H_3S$  *thienyl*, by contraction of thiophenyl, to distinguish it from other phenyl derivatives containing sulphur.

*Simple Condensation-products of Thiophene.*—Like aromatic hydrocarbons, thiophene gives condensation-products. With chloral in presence of glacial acetic acid and sulphuric acid, a crystalline substance,  $CCl_3CH : (C_4H_3S)_2$ , is formed; a similar compound with bromal; and with methylal, a compound dithienylmethane, so closely resembling diphenylmethane as to have even the same strong characteristic smell of oranges, are formed. Almost all the thiophene derivatives give the blue colour due to the formation of indophenine when heated with isatin and sulphuric acid. Thiophene reacts with benzyl chloride, benzoic chloride, and phthalic chloride in presence of aluminium chloride, due regard being paid to the prevention of formation of sulphuretted hydrogen; with benzoic chloride it forms for example phenylthienyl ketone,  $Ph.CO.C_4H_3S$ , analogous to diphenyl ketone. This derivative yields with hydroxylamine the isonitroso-compound  $CPh(NO.H).C_4H_3S$ , which latter, when heated with soda-lime, breaks up directly into benzoic acid and thiophene. The investigation of similar consequential reactions is in process.

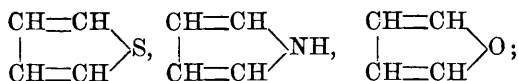
*Homologues of Thiophene.*—Owing to the difficulty of obtaining the monobromo-derivative of thiophene, Fittig's synthesis, which doubtless otherwise would be found applicable, has not been available for the formation of methylthiophene. As, however, the purest toluene obtained from tar contains some sulphur, the presence of methylthiophene was suspected (*Abstr.*, 1884, 45), and on treatment of 2000 kilos. in a manner similar to that by which thiophene was obtained from benzene (*Abstr.*, 1883, 1091), it was extracted. The pure substance has not yet been isolated, but dibromomethylthiophene,  $C_4HBr_2Me$ , has been obtained chemically pure, and is an oil similar in character to aromatic dibromo-derivatives, boiling at  $227-229^{\circ}$ . The corresponding thiophenes may be expected to be obtained from coal-tar xylene, and cumene. Thiophene also yields a large number of dye-stuffs. The violet dye-stuff obtained by the action of phenylglyoxylic acid on benzene is due to the presence of thiophene. As a general rule, ketones which consist only of carbon, hydrogen, and oxygen, give dye-stuffs with thiophene if they contain the group  $CO.CO$ ; simple ketones, or double ketones which do not contain the two carbonyl groups as above, do not. Phenanthraquinone yields a violet dye-stuff,  $C_{19}H_{12}SO$ , with methylthiophene, and with thiophene a green dye-stuff, insoluble in ether, benzene, light petroleum, and

concentrated sulphuric acid, but soluble in chloroform. Dibenzoyl and thiophene give a blue, and alloxan and thiophene a deep-blue dye-stuff; on the other hand, phenyl methyl ketone (acetophenone), diphenyl ketone (benzophenone), anthraquinone, &c., give none. Phenanthraquinone, as an ortho-diketone, yields a dye-stuff, whilst anthraquinone does not. Thiophene also yields dye-stuffs with isatin, benzoyl cyanide, &c., and various aldehydes (with benzaldehyde a deep blue); but the formation of these is due to a more complicated condensation than the above. The intensity of the dye-stuff formed depends on the chromogenic nature of the substance containing the group CO.CO. Thus with compounds of the aromatic series or of the uric acid group, the colours are beautiful and deep, whilst this is less the case with compounds of the paraffin series.

*Thiophenesulphonic Acid*.—In conjunction with Weitz the author has prepared numerous derivatives of this acid, some of which have been already described (Abstr., 1884, 45), and at present they are investigating the sulphinic acid derivative,  $C_4H_3S.SO_2H$ , and the mercaptan,  $C_4H_3S.SH$ ; the latter is of special interest, as the corresponding compound,  $C_4H_3S.OH$ , has not yet been obtained.

*Coal-tar Dyes containing Nitrogen*.—From a coal-tar oil distilling between  $90^\circ$  and  $109^\circ$ , the author has also obtained with isatin and dilute sulphuric acid a deep blue dye-stuff, which has been found to be due to the presence of pyrroline. The same dye-stuff has been obtained with ease from pure pyrroline. It is an indigo-blue powder, soluble in acetic acid, but only sparingly in alcohol, ether, and concentrated sulphuric acid.

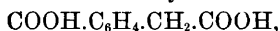
From these and other properties the author considers that thiophene, pyrroline, and furfuran (*Ber.*, 16, 1476) must be considered analogous, as shown by the graphic formulæ:—



also that they are related to benzene by the replacement of one of the three acetylene-groups which form the benzene molecule by S, NH, or O, and that this takes place without obliterating the peculiar characteristics of benzene and its derivatives.

A. B.

**Oxidation of Diethylbenzene.** By ALLEN and UNDERWOOD (*Bull. Soc. Chim.*, 40, 100—101).—The diethylbenzene boiling at  $176^\circ$ — $179^\circ$ , obtained as one of the products of the action of ethyl chloride on benzene in presence of aluminium chloride, if submitted to partial oxidation with chromic acid mixture yields an acid,



crystallising in white needles, which sublime without melting at  $200^\circ$ — $210^\circ$ . By more prolonged oxidation of this acid, or by oxidation of the original hydrocarbon with potassium permanganate, the [1:3] phthalic acid is formed. Further experiments on the relation between the diethylbenzene and of these acids derived from it are promised.

V. H. V.

**Preparation of Mesitylene.** By E. VARENNE (*Bull. Soc. Chim.*, **40**, 266—267).—Attempts to convert acetone into mesitylene by the action of zinc chloride under different conditions led to negative results. A good yield was obtained by treating 180 grams of acetone with 300 grams of strong sulphuric acid for an hour. The liquid is then heated in a flask until it begins to froth up, when it is distilled in a current of steam; 40 grams of mesitylene were obtained from the distillate.

W. C. W.

**Bromine Derivatives.** By V. MERZ and W. WEITH (*Ber.*, **16**, 2890—2896).—Chloranil is comparatively readily converted into perchlorobenzene by the action of phosphorus pentachloride (*Annalen*, **146**, 12), whilst the analogous conversion of bromanil into perbromobenzene is found to require a much higher temperature (260—280°), and to be even then very incomplete. Perbromobenzene is more readily obtained by heating pentabromophenol with phosphorus pentabromide. Berthelot and Jungfleisch showed that acetylene tetrachloride is decomposed at 360° into perchlorobenzene and hydrochloric acid. On heating acetylene tetrabromide in a sealed tube at 300°, it becomes carbonised, a trace of a substance being, however, obtained which does not melt at 300°, and is probably perbromobenzene. On heating benzonitrile with bromine containing iodine at about 350°, it is converted into perbromobenzonitrile; this is very sparingly soluble in boiling alcohol or ether, and is not readily dissolved by hot benzene or carbon bisulphide. It melts above 300°, and sublimes with slight carbonisation in the form of long slender needles; it is no less stable than the corresponding chlorine derivative, hydrochloric acid at 200° having scarcely any action on it, although alcoholic alkali at 180—200° slowly decomposes it with formation of ammonia and metallic chloride. By the action of an excess of bromine on potassium ferro- and ferri-cyanides, an abundant yield of cyanuric bromide is produced, from which pure cyanuric acid can be readily obtained. When ferrocyanide is employed, it should be heated with 10 times its weight of bromine for 8—10 hours at 200—220°, whilst in the case of potassium ferricyanide 6 parts of bromine are recommended, the mixture being heated for 5—6 hours at about 220°.

A. K. M.

**Exhaustive Chlorination of Aromatic Substances. I.** By V. MERZ and W. WEITH (*Ber.*, **16**, 2869—2889).—Ruoff showed that the energetic chlorination of diphenyl yields perchlorodiphenyl and not perchlorobenzene (*Ber.*, **9**, 1491). Phenanthrene on the other hand, although a diphenyl-derivative, is converted into perchlorobenzene. In the case of certain diphenyl-derivatives, different results were, however, obtained, being affected apparently either by the way in which the chlorination is carried out, or by the presence of impurities. The chlorination is effected by treating the substance with a large excess of antimony pentachloride, and after the reaction (if any) has ceased, heating the mixture gradually up to 360°, and maintaining it at this temperature until no more hydrochloric acid is liberated. If antimony pentachloride acts too violently, the substance is first treated with chlorine, and subsequently with the pentachloride. At the end



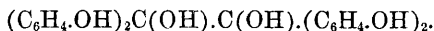
of the reaction, the decomposed pentachloride is renewed, and the mixture again heated to insure complete chlorination. Treated in this way, phenanthraquinone (unlike phenanthrene) is converted almost entirely into perchlorodiphenyl with formation of very little perchlorobenzene. Diphenic acid yields similar results, although a somewhat larger proportion of perchlorobenzene, whilst in the case of diphenyleneglycollic acid, a large proportion of perchlorodiphenyl was obtained in some experiments, and in others a considerable amount of perchlorobenzene. Similar differences were observed with carbazol, but as a rule the perchlorobenzene is largely in excess of the perchlorodiphenyl, although under certain conditions the latter alone is produced. Benzidine yields principally perchlorobenzene with very little perchlorodiphenyl. Ditolyl yields perchlorodiphenyl and perchloromethane, whilst dibenzyl, trimethylmethane, and diphenylenephénylmethane yield perchlorobenzene. Diphenyleneacetic acid and fluorene could not be completely decomposed, perchlorofluorene being apparently the chief product. The chlorination of rosaniline and violaniline is also very incomplete, very little perchlorobenzene being formed whilst the product still contained nitrogen. Chrysene is comparatively readily acted on and yields perchloromethane, perchlorethane, and perchlorobenzene; pyrene on the other hand offers a greater resistance to the action of chlorine, and yields perchloromethane and the two compounds  $C_{15}Cl_{10}$  and  $C_{14}Cl_{10}$ . Diphenylbenzene and triphenylbenzene are converted into the corresponding chlorine-derivatives,  $C_{18}Cl_{14}$  and  $C_{24}Cl_{18}$ , the former separating from hot nitrobenzene in crystalline grains, the latter in needles. Benzonitrile yields perchlorobenzonitrile,  $C_6Cl_5.CN$ , on chlorination, whilst  $\beta$ -naphthonitrile yields perchlorobenzene. Perchlorobenzonitrile is sparingly soluble in cold alcohol or ether, readily in boiling alcohol, from which it crystallises in clusters of colourless needles, also in carbon bisulphide and chloroform. It melts at  $210^\circ$ , is not acted on by hydrochloric acid even at  $200^\circ$ , but is decomposed when heated with alcoholic soda with formation of ammonia and metallic chloride; perchlorobenzene and perchlorodiphenyl are also decomposed when treated with alcoholic soda. From the above results, it is seen that certain diphenyl-derivatives yield perchlorobenzene, and practically no perchlorodiphenyl. From the chlorination of the immediate derivatives of benzene, no perchlorodiphenyl is produced. The formation of perchlorodiphenyl by perchlorination would seem to indicate the pre-existence of a diphenyl-substance, and the reaction will at any rate in some cases throw light on the constitution of aromatic compounds.

A. K. M.

**Methyl Ethers of Phenol.** By C. VINCENT (*Bull. Soc. Chim.*, **40**, 106—107).—In order to convert the phenols into their corresponding methyl ethers, the sodium or potassium phenate is heated in a rapid current of commercial methyl chloride. For example, phenol is thus converted into anisöl, together with smaller quantities of methylparacresol derived from impurities of the phenol. Similarly,  $\alpha$ - or  $\beta$ -naphthol is converted into the corresponding  $\alpha$ - or  $\beta$ -methyl naphthol ether.

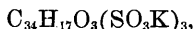
This process is to be recommended for its simplicity of execution, and the purity of the products thereby formed. V. H. V.

**Condensation of Aromatic Aldehydes with Phenols.** By W. TRZCINSKI (*Ber.*, 16, 2835—2841).—According to Baeyer and his pupils, aldehydes of the paraffin series unite with phenols in the proportion of 1 mol. to 2, whilst with aromatic aldehydes they unite in equal molecular proportions (*Ber.*, 5, 25, 280, 1094; 6, 220; 7, 1181). By the action of salicylaldehyde on phenol, Liebermann (*Ber.*, 9, 800; 11, 1436) obtained a substance the composition of which differed entirely from that indicated in either of the equations:  $2C_7H_6O_2 + 2C_6H_6O - H_2O = C_{26}H_{22}O_5$ , or  $C_7H_6O_2 + 2C_6H_6O - H_2O = C_{19}H_{16}O_3$ , and from parahydroxybenzaldehyde and phenol he obtained a compound,  $C_{26}H_{22}O_5$ , which he imagined to be formed thus:  $2C_7H_6O_2 + 2C_6H_6O + O = C_{26}H_{22}O_5 + H_2O$ , and to have the constitution—



By heating parahydroxybenzaldehyde (5 parts) with  $\beta$ -naphthol (12 parts) and concentrated sulphuric acid (50 parts) on a water-bath, the author has prepared an orange-yellow crystalline and very stable compound, which is the trisulphonic acid of a condensation-product of the formula  $C_{34}H_{20}O_3$ . On treating the product with water, *melinointrisulphonic acid* is obtained in yellow flakes. It yields a calcium salt readily soluble in hot water, and on decomposing this with hydrochloric acid, a yellow precipitate is produced which is a compound of the new substance with hydrochloric acid. Melinointrisulphonic acid is insoluble in absolute alcohol, moderately soluble in water. In thin layers it is pink with a green fluorescence, and in thicker layers pure yellow. Concentrated sulphuric and nitric acids dissolve it readily with green fluorescence; but it is precipitated from its aqueous solution by mineral acids. In alkaline solution it can be reduced by zinc-dust, and on treating the filtrate with hydrochloric acid, the reduction-product separates in brownish-red, concentrically grouped prisms, which readily oxidise to the original substance.

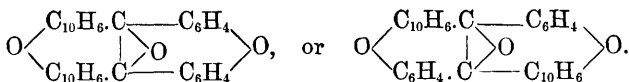
Melinointrisulphonic acid does not melt at  $300^\circ$ ; it is a powerful acid, forms colourless solutions with the alkalis, and is not precipitated from its salts by dilute acetic acid. The potassium salt,



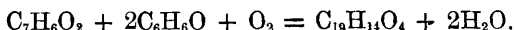
forms slender colourless needles readily soluble in water, sparingly in alcohol; it contains water of crystallisation, which it loses in the desiccator. The calcium salt  $(C_{34}H_{17}O_3)_2(S_2O_6Ca)_3$ , also forms colourless needles containing water of crystallisation, whilst the barium salt,  $(C_{34}H_{17}O_3)_2(S_2O_6Ba)_3$ , is obtained as an amorphous precipitate, or from very dilute solutions in microscopic needles. The ammonium salt crystallises in slender silky colourless needles, readily soluble in water.

Melinointrisulphonic acid is also formed when  $\beta$ -naphtholsulphonic acid is employed in the place of naphthol, but cannot be produced from salicylaldehyde and  $\beta$ -naphthol, nor from parahydroxybenzaldehyde and  $\alpha$ -naphthol, nor from  $\beta$ -dinaphthol and parahydroxybenzaldehyde.

It is, however, produced on heating bitter almond oil with  $\beta$ -naphthol and sulphuric acid at  $200-220^\circ$ , this being the most economical method of preparing it in quantity. Disregarding the sulphonic groups, the author regards the constitution as represented by one of the following formulæ:—



The composition of the substance obtained from salicylaldehyde and phenol shows that oxidation occurs in these condensations besides the separation of water. The author has prepared this compound by the method employed by Liebermann (*Ber.*, **11**, 1437), and obtained a dye-stuff which does not form a crystalline product with hydrochloric acid, its alkaline solution having a more violet shade than aurin. From its formula,  $\text{C}_{19}\text{H}_{14}\text{O}_4$ , the author names it oxyaurin, and explains its formation by the following equation:—



A. K. M.

**Action of Aniline on Resorcinol and Quinol.** By A. CALM (*Ber.*, **16**, 2786—2814).—When resorcinol (1 mol.) is heated with aniline (4 mols.) and anhydrous calcium chloride (2 mols.) for 8 hours at  $270-280^\circ$ , *metahydroxydiphenylamine*,  $\text{C}_6\text{H}_4(\text{OH})\text{NHPH}$ , is formed and can be separated either by solution in hydrochloric acid and subsequent precipitation of the base, or by distillation with superheated steam. It crystallises in white nacreous scales, melts at  $81.5-82^\circ$ , and distils at about  $340^\circ$ ; it dissolves in large quantities of water and also in acids and in alkalis with formation of salts, the hydrochloric acid solution yielding a yellowish crystalline precipitate with platinic chloride. It is also readily soluble in wood spirit, alcohol, ether, acetone, and benzene, sparingly in light petroleum; it dissolves in pure concentrated sulphuric acid without coloration, but a little nitric acid colours the solution deep red-brown; sodium nitrite produces a yellowish-green, and manganese dioxide a bluish-violet coloration. *Metahydroxydiphenylamine* is reduced by distillation with zinc-dust to diphenylamine. *Metahydroxydiphenylamine sulphate*,  $(\text{C}_{12}\text{H}_{11}\text{NO})_2\text{H}_2\text{SO}_4$ , crystallises in lustrous needles, and is rapidly decomposed by water or alcohol. The *hydrochloride*,  $\text{C}_{12}\text{H}_{11}\text{NO}\cdot\text{HCl}$ , forms readily decomposable small white needles. The potassium and sodium derivatives crystallise from warm concentrated alkali in colourless needles; their solutions yield precipitates with the alkaline earths and heavy metals. The *barium derivative*,  $(\text{C}_{12}\text{H}_{10}\text{NO})_2\text{Ba}\cdot 5\text{H}_2\text{O}$ , forms crystalline scales soluble in water and in alcohol.

*Metahydroxydiphenylamine* is also produced when resorcinol and aniline are heated together at a high temperature. To prepare *diphenylmetaphenylenediamine*,  $\text{C}_6\text{H}_4(\text{NHPH})_2$ , the resorcinol (1 mol.) is best heated with aniline (4 mols.), calcium chloride (3—4 mols.), and zinc chloride ( $\frac{1}{2}$  mol.) for 30—40 hours at about  $210^\circ$ , and the product treated with glacial acetic or hydrochloric acid, the hydroxy-

diphenylamine being separated by washing with water and treatment with alkali. It forms colourless needles melting at  $95^{\circ}$ , is insoluble in water, dilute acids, and alkalis, slightly soluble in concentrated hydrochloric acid, readily in concentrated sulphuric acid; it is readily soluble in ether and hot benzene, less so in cold benzene and hot alcohol, sparingly in cold alcohol, and warm light petroleum. Its colourless solution in sulphuric acid becomes yellowish-green, and then bluish-violet on addition of potassium nitrate or nitric acid, whilst sodium nitrite produces a reddish violet-blue coloration. Potassium dichromate produces a greenish and then a bluish-violet coloration, the latter colour being also produced on warming the sulphuric acid solution with manganese dioxide.

*Diphenylmetaphenylenediamine hydrochloride*,  $C_6H_4(NHPh, HCl)_2$ , is obtained by passing dry hydrochloric acid into a solution of the diamine in benzene. The *acetyl-derivative*,  $C_6H_4(NPhAc)_2$ , is sparingly soluble in cold alcohol and ether, more readily in benzene and in chloroform, very sparingly in water and light petroleum; it melts at  $163^{\circ}$ . The *benzoyl-derivative*,  $C_6H_4(NPhBz)_2$ , melts at  $184^{\circ}$ , is readily soluble in hot benzene and in chloroform, less so in hot alcohol and in ether, sparingly in cold alcohol and in light petroleum. *Di-n-troso-diphenylmetaphenylenediamine*,  $C_6H_4(NPh.NO)_2$ , is obtained on adding hydrochloric acid to an alcoholic solution of diphenylmetaphenylenediamine and then gradually sodium nitrite. It crystallises in needles melting at  $102^{\circ}$ , and is readily soluble in alcohol, ether, benzene, and glacial acetic acid, almost insoluble in light petroleum. It dissolves in concentrated sulphuric acid with a very characteristic violet-blue coloration, whilst with phenol and sulphuric acid it yields a bluish-violet coloration gradually changing to green.

To prepare *parahydroxydiphenylamine*,  $C_6H_4(OH).NHPh$ , quinol (1 mol.) is heated with aniline (4 mols.) and calcium chloride (2 mols.) for 8–10 hours at  $250$ – $260^{\circ}$ . It crystallises in scales melting at  $70^{\circ}$ , and boils at  $330^{\circ}$ . Pure concentrated sulphuric acid dissolves it almost without coloration, but the addition of nitric acid colours the solution brownish-yellow to brownish-red. It is readily soluble in methyl and ethyl alcohols, ether, chloroform, and warm benzene and toluene, sparingly in hot water, very slightly in cold water and in light petroleum; it also dissolves in acid and alkaline solutions. When distilled with zinc-dust it is converted into diphenylamine. *Parahydroxydiphenylamine hydrochloride*,  $C_{12}H_{11}NO, HCl$ , crystallises in white needles which become greenish by exposure to light. The derivatives of the alkali and alkaline earth-metals are more readily soluble and less crystalline than the corresponding derivatives of the meta-compound. Parahydroxydiphenylamine can likewise be obtained by heating quinol with aniline for 16 hours at  $290$ – $300^{\circ}$ , in which case it is accompanied by a second substance which is insoluble in hydrochloric acid. *Diphenylparaphenylenediamine*,  $C_6H_4(NHPh)_2$ , can be most conveniently prepared by heating quinol and aniline with a mixture of zinc and calcium chlorides by themselves (see above) for 18 hours at  $200$ – $210^{\circ}$ . Diphenylparaphenylenediamine forms colourless lustrous scales melting at  $152^{\circ}$ , and distilling unchanged at a high temperature. It is readily soluble in warm benzene, toluene, glacial

acetic acid, ether, and chloroform, less readily in even warm alcohol, very sparingly in light petroleum, and is practically insoluble in dilute acids. It forms a colourless solution with pure concentrated sulphuric acid, the addition of nitric acid, potassium nitrate, or sodium nitrite producing a splendid red coloration; chlorine-water produces the same colour, whilst bromine-water colours the solution reddish-violet, then bluish-violet; manganese dioxide colours the solution violet to violet-blue. Fuming nitric acid in small quantity gives a blood-red coloration with the diamine. *Diphenylparaphenylenediamine hydrochloride*,  $C_6H_4(N_2H_5) \cdot 2HCl$ , is obtained partly in the form of slender white needles and partly as a granular crystalline greyish-white mass, and is readily decomposed by water. The *acetyl-derivative*,

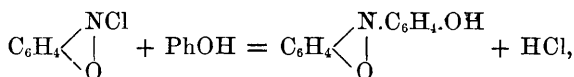


crystallises in small plates or prisms melting at  $191.7^\circ$ ; it dissolves readily in warm benzene and in chloroform, less so in hot alcohol, sparingly in cold benzene, alcohol, and light petroleum, and is insoluble in water. The *benzoyl-derivative*,  $C_6H_4(NPh\overline{Bz})_2$ , melts at  $218.5^\circ$ , is moderately soluble in hot benzene, toluene, amyl alcohol, and chloroform, sparingly in cold benzene, and very sparingly in light petroleum, cold alcohol, and ether. The *dinitroso-derivative*,  $C_6H_4(NPhNO)_2$ , forms golden-yellow scales sparingly soluble in alcohol, ether, glacial acetic acid, benzene, and light petroleum; the alcoholic solution becomes deep red when heated, probably from decomposition. Powerful reducing agents convert it into diphenylparaphenylenediamine. The nitroso-compound is coloured red by pure sulphuric acid, the colour becoming more violet in the presence of phenol.

On heating parahydroxydiphenylamine with paratoluidine, and calcium and zinc chlorides, with the view to produce paratolylphenylparaphenylenediamine,  $C_6H_4Me.NH.C_6H_4.NHPh$ , a different result was obtained, a substance being formed agreeing in composition and properties with *diparatolylparaphenylenediamine*,  $C_6H_4(NH.C_6H_4Me)_2$ , prepared from quinol and paratoluidine. Diphenylparaphenylenediamine is also produced.

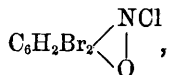
A. K. M.

**Indophenol-like Dyes and Indophenols.** By R. MÖHLAU (*Ber.*, 16, 2843—2857).—From differences in composition and properties, the author divides these substances into two classes: he suggests that the former (indophenol-like dyes) should be termed indophenols from their pronounced phenol character, and the latter *indoanils*, indicating their derivation from aniline. The first group contains the colouring substances first mentioned by Hirsch (*Ber.*, 13, 1909), and which may be obtained thus: By the action of quinonechlorimides on phenols, and by the oxidation of a paramidophenol and a phenol in molecular proportions. The view that the action of quinonechlorimide on phenol took place as in the equation

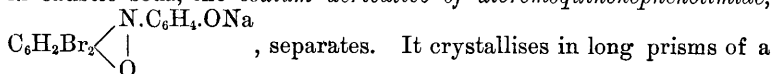


was not confirmed by Hirsch, as he was unable to isolate the quinone-

phenolimide, and the author has therefore examined the reaction, employing dibromoquinonechlorimide in the hopes of obtaining crystallisable products. To prepare *dibromoquinonechlorimide*,



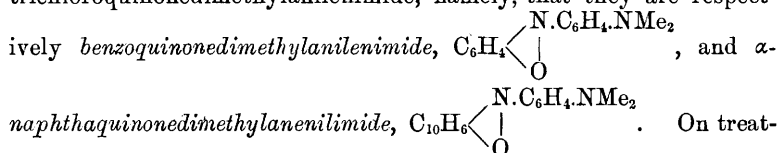
dibromoparamidophenol, from the corresponding paranitrophenol, is treated with chloride of lime in the usual way. The product crystallises from alcohol or glacial acetic acid in long dark yellow prisms melting at  $80^\circ$ , and decomposing at  $121^\circ$ . On introducing dibromoquinonechlorimide, mixed with dilute alcohol, into solution of phenol in caustic soda, the *sodium derivative of dibromoquinonephenolimide*,



splendid golden-green lustre, but is blue by transmitted light, and yields blue solutions with water and alcohol. On warming it with dilute soda solution, the colour changes to pale red, probably from the formation of the compound  $\text{C}_6\text{H}_2\text{Br}_2(\text{ONa}).\text{N}(\text{OH})\text{C}_6\text{H}_4.\text{ONa}$ . *Dibromoquinonephenolimide* is obtained on gradually adding acetic acid to a warm aqueous solution ( $60^\circ$ ) of the sodium derivative. It crystallises in dark red, almost black, prisms of metallic lustre, yields red solutions with alcohol, ether, and glacial acetic acid, but is insoluble in water. By the action of strong mineral acids it yields *dibromoparamidophenol* and *quinone*. When an alkaline solution of the sodium derivative of dibromoquinonephenolimide is warmed with glucose, the colour disappears, owing to the formation of the sodium salt of a leuco-derivative, which, from its solubility and from the readiness with which it becomes oxidised, is very difficult to isolate. *Leuco-dibromoquinonephenolimide*,  $\text{C}_6\text{H}_2\text{Br}_2(\text{OH}).\text{NH.C}_6\text{H}_4.\text{OH}$ , is, however, readily obtained in colourless prisms on passing sulphurous anhydride into a warm aqueous solution of the sodium salt; it dissolves readily in the usual solvents, water excepted, and melts at  $170^\circ$  with darkening. If the reaction between dibromoquinonechlorimide and phenol be a typical process, it proves the correctness of Hirsch's view. The colour-reactions produced by the union of dibromoquinonechlorimide with other phenols in alkaline solution, and the behaviour of dibromoquinonephenolimide towards mineral acids, show that it is the hydrogen-atom in the para-position to the hydroxyl of the phenol which is eliminated by the chlorine-atom of the chlorimides. Dibromoquinonephenolimide can also be obtained by dissolving dibromamidophenol, and phenol in caustic soda solution, and oxidation with potassium dichromate. Dibromamidophenol crystallises from alcohol in lustrous prisms, melts at  $180^\circ$ , is soluble in dilute acids, and much more readily soluble in alkalis.

The indophenols (indoanils) are distinguished from the above by not yielding soluble salts with the alkalis, whilst they show a more or less distinctly basic character, due to the presence of a tertiary amido-group. Phenol-blue and  $\alpha$ -naphthol-blue can be prepared by the action of nitrosodimethylaniline on phenol, and on  $\alpha$ -naphthol in alka-

line solution at the ordinary temperature, especially in the presence of reducing agents; also by the oxidation of dimethylparaphenylenediamine and phenol (or  $\alpha$ -naphthol) under like conditions. Trichloroquinonedimethylanilenimide, which, according to the author, also belongs to this class of substances, is formed by the action of trichloroquinonechlorimide on dimethylaniline, and from the resemblance in its properties to those of phenol-blue and  $\alpha$ -naphthol-blue, the author assumes that these have an analogous constitution to that of trichloroquinonedimethylanilenimide, namely, that they are respectively



ing indophenol paste ( $\alpha$ -naphthol-blue) with hydrochloric acid a dark yellow solution is obtained, which soon solidifies to a grey jelly, and on agitating this with ether,  $\alpha$ -naphthaquinone is extracted, whilst dimethylparaphenylenediamine hydrochloride remains in the acid solution. Phenol-blue treated in the same way yields benzoquinone and dimethylparaphenylenediamine. A. K. M.

**Crystalline Bases of Methyl-violet.** By H. WICHELHAUS (*Ber.*, 16, 3044—3045).—A question of priority.

**Constitution of Methylene-blue.** (Preliminary notice.) By E. ERLENMEYER (*Ber.*, 16, 2857—2858).—According to the author's views Bindschedler's green has the constitution



By the action of hydrogen sulphide on this, he thinks that the compound  $\text{NMe}_2.\text{C}_6\text{H}_4.\text{NH}.\text{CH}_2.\text{NMe}.\text{C}_6\text{H}_4.\text{SH}$  may possibly be formed, which, by the action of ferric chloride, is converted into methylene-blue,  $\text{NMe}_2.\text{C}_6\text{H}_4.\text{N} < \begin{array}{c} \text{CH}_2 \\ | \\ \text{S.C}_6\text{H}_4 \end{array} > \text{NMe}$ . Methylene-white is assumed to have the constitution  $\text{NMe}_2.\text{C}_6\text{H}_4.\text{NH}.\text{S}.\text{C}_6\text{H}_4.\text{NMe}_2$ . The author thinks it improbable that the sulphur-atom in methylene-blue occupies a position between two nitrogen-atoms, as assumed by Möhlau.

A. K. M.

**Methylene-blue and Allied Dye-stuffs.** By A. BERNTHSEN (*Ber.*, 16, 2896—2904).—The close relation between methylene-blue and Laut's violet obtained from paraphenylenediamine is indicated by analytical results, and if the formula  $\text{C}_{24}\text{H}_{20}\text{N}_6\text{S}_2$  be halved and modified to  $\text{C}_{12}\text{H}_9\text{N}_3\text{S}$ , in accordance with the law of even numbers, it would seem probable that methylene-blue is homologous with Laut's violet, and that its formula is  $\text{C}_{16}\text{H}_{17}\text{N}_3\text{S}$ , and not  $\text{C}_{16}\text{H}_{19}\text{N}_3\text{S}$ , as previously supposed by the author. By heating a mixture of diphenylamine and sulphur (10:4) at 250—300°, hydrogen sulphide is evolved and *thiodiphenylamine*,  $\text{C}_{12}\text{H}_9\text{NS}$ , obtained. This appears to be the

parent substance to the above dye-stuffs, the leuco-violet being probably a *diamidothiodiphenylamine*, and the leuco-blue a *tetramethyldiamidothiodiphenylamine*. Thiodiphenylamine crystallises from alcohol in pale yellow lustrous plates; it is moderately soluble in cold ether, sparingly in cold alcohol, glacial acetic acid, and benzene, although more readily when heated. It has no basic properties, melts at  $180^{\circ}$ , and can be distilled almost unchanged, its boiling point being about  $371^{\circ}$ ; its vapour-density (determined in nitrogen) agrees with the formula given. It is oxidised by exposure to air, its alcoholic solution assuming a red coloration, whilst ferric chloride and bromine vapour produce a green coloration. Solid thiodiphenylamine is coloured brownish-red by nitrous acid. It forms a greenish-brown solution with cold concentrated sulphuric acid, from which water throws down a crystalline precipitate. The following is a characteristic and delicate reaction: the substance is treated with a few drops of fuming nitric acid, water added, and the product boiled with acid stannous chloride solution. The tin is then thrown down by means of zinc, and an excess of ammonia added, when the solution soon assumes an intense violet coloration from the absorption of oxygen. If ferric chloride is added after removing the tin, a reddish-violet precipitate is produced if the solution is concentrated, and a violet coloration if dilute. *Acetylthiodiphenylamine*,  $C_{12}H_9NSAc$ , prepared by boiling thiodiphenylamine with excess of acetic anhydride, is sparingly soluble in hot glacial acetic acid, alcohol, and benzene, and crystallises from alcohol in thin glistening prisms. It resembles thiodiphenylamine in its behaviour to sulphuric acid, and in giving the above colour reaction. *Methylthiodiphenylamine*,  $C_{12}H_9NSMe$ , obtained on heating thiodiphenylamine with methyl iodide and methyl alcohol at  $100-110^{\circ}$ , forms magnificent long prisms, is moderately soluble in cold alcohol and ether, readily in hot alcohol, melts at  $99.3^{\circ}$ , and volatilises at higher temperatures almost unchanged. It yields a greenish-brown solution with sulphuric acid, and with nitric acid a bright yellow nitro-derivative; when this is treated with stannous chloride and hydrochloric acid, a product is obtained crystallising in white needles. *Ethylthiodiphenylamine*,  $C_{12}H_9NSEt$ , melts at  $102^{\circ}$ , and crystallises from hot alcohol in long thin white prisms. The formula of thiodiphenylamine is probably  $C_6H_4<\underset{S}{\overset{NH}{-}}>C_6H_4$ . By the oxidation of its methyl-derivative by potassium permanganate, a substance,  $C_{13}H_{11}NSO_2$ , is obtained, which is probably *methyldiphenylaminesulphone*. It is sparingly soluble in alcohol, ether, and glacial acetic acid, insoluble in water; it melts at about  $222^{\circ}$ , has neither basic nor acid properties, and is not altered by boiling concentrated potash, nor by hydrochloric acid. On heating it with concentrated sulphuric acid, a blue solution is obtained, and on pouring this into water, the colour changes to brownish-violet.

The close relationship of thiodiphenylamine to Laut's violet and to methylene-blue is indicated by the following considerations: Thiodiphenylamine is very readily acted on by nitric acid with formation of a dinitro-derivative, soluble in alkalis and in strong ammonia. On treating the nitro-derivative with acid stannous chloride solution, a



colourless liquid is obtained containing the tin double salt of a leuco-base, and by the oxidation of this a violet dye-stuff is produced which bears a very close resemblance to Laut's violet. Instead of treating diphenylamine with sulphur, and subsequently introducing amido-groups, experiments are being made with the view to obtain violet and blue dye-stuffs by the introduction of sulphur into amidodiphenylamines. On reducing a slightly acid solution of dimethylphenylene-green,  $C_{16}H_{13}N_3$ , by hydrogen sulphide to *tetramethyldiamidodiphenylamine*, and then oxidising by means of ferric chloride, a green coloration is at first produced, but soon changes to blue-green with separation of sulphur, and finally to blue, the product containing methylene-blue.

A. K. M.

**Preparation of Phenylhydrazine.** By V. MEYER and M. T. LECCO (*Ber.*, 16, 2976).—Phenylhydrazine hydrochloride is easily obtained by the action of stannous chloride and hydrochloric acid on diazobenzene chloride,  $PhN:N.Cl + 3HCl + 2SnCl_2 = 2SnCl_4 + NHPPh.NH_2$ . It may be obtained direct from aniline by dissolving 10 grams aniline in 200 grams concentrated hydrochloric acid, and slowly adding to the cooled solution 7.5 grams sodium nitrite dissolved in 50 c.c. water, and afterwards 45 grams stannous chloride dissolved in 41.5 grams concentrated hydrochloric acid. The reaction takes place at once, and a white crystalline mass of the salt is obtained. By decomposing this with alkali and exhausting with ether the pure base may be obtained in the crystalline state.

A. B.

**Action of Aldehydes on Phenols.** (I.) By A. MICHAEL (*Amer. Chem. J.*, 5, 339—349).—Benzaldehyde and resorcinol may be heated together in closed vessels for days without any reaction occurring; heated in sealed tubes at  $200^\circ$  a resinous substance is formed. In the presence of acids, on the contrary, the substances react with great readiness. The addition of one drop of hydrochloric acid to a solution of 1 gram resorcinol and 1 gram benzaldehyde in 3 grams absolute alcohol causes the temperature to rise to  $55\text{--}60^\circ$ , and a crystalline deposit is formed. The filtered alcoholic liquid is poured into water, when a white resin is precipitated; this cannot be crystallised, and assumes a reddish tinge if dried in a current of carbonic anhydride; analysis gave numbers agreeing with the formula  $C_{26}H_{20}O_4$ . It is readily soluble in alcohol, benzene, ether, and glacial acetic acid, and also in alkalis. It melts at about  $330^\circ$  with decomposition. The acetyl-derivative,  $C_{26}H_{16}O_4Ac_4$ , which is white and amorphous, is somewhat less soluble than the resin. The crystalline deposit mentioned above is formed by the action of acids on the resin; it is best prepared by heating 5 parts of benzaldehyde and 10 parts of resorcinol in 20 parts of water on the water-bath, and then adding a few cubic centimeters of very dilute hydrochloric acid. It consists of two substances, one crystallising in square plates, the other in needles. The former, which is separated by extracting the deposit with alcohol, has the formula  $C_{26}H_{20}O_4 + 4H_2O$ , melts with decomposition at above  $330^\circ$ , is moderately soluble in hot, sparingly soluble in cold alcohol, insoluble in water and ether. It dissolves in alkalis, and is reprecipi-

tated by acids in the amorphous form. On fusion with potash it yields resorcinol and benzoic acid. The acetyl-derivative,



crystallises in obliquely truncated, translucent prisms, insoluble in cold, sparingly soluble in hot alcohol. The second substance obtained by the action of acids on the resin is only obtained in small quantity; it crystallises in needles, and is only very slightly soluble in hot alcohol. The conversion of resorcinol and benzaldehyde into a resin is effected also by small quantities of other acids, such as sulphuric, phosphoric, acetic, oxalic acids, &c., also by the fixed alkalis and potassium carbonate.

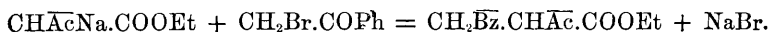
A. J. G.

**Action of Aldehydes on Phenols. (II.)** By A. MICHAEL and A. M. COMEY (*Amer. Chem. J.*, **5**, 349—353).—The addition of a drop of hydrochloric acid to a mixture of acetaldehyde and orcinol at 100° causes an abundant precipitate of small round plates of a substance of the formula  $\text{C}_{18}\text{H}_{20}\text{O}_4$ . It is insoluble in the ordinary organic solvents, but is soluble in alkalis, the solution rapidly oxidising on exposure to air. Resorcinol gives a similar substance, which could not, however, be obtained in a state fit for analysis.

Five parts of chloral hydrate, 10 parts resorcinol, and 40 parts of water were heated for 12—24 hours in a flask provided with a reflux condenser; a crystalline product separates which, after purification, forms fine yellowish needles of the formula  $\text{C}_8\text{H}_6\text{O}_3$ , somewhat soluble in hot water, readily soluble in hot alcohol and acetic acid. Its solution in concentrated sulphuric acid assumes a fine blue colour on exposure to air. Potassium permanganate completely oxidises it to carbonic anhydride. The acetyl-derivative,  $\text{C}_8\text{H}_4\text{O}_3\text{Ac}_2$ , forms white prismatic crystals melting at 120°. The benzoyl-derivative,  $\text{C}_8\text{H}_4\text{O}_3\text{Bz}_2$ , is obtained in small crystals of a slight pinkish tint melting at 165°. Chloral hydrate and orcinol yield a similar compound melting at 250°, whose acetyl-derivative melts at 150°.

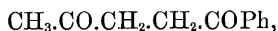
A. J. G.

**Action of Bromacetophenone on Ethyl Sodacetoacetate.** By C. PAAL (*Ber.*, **16**, 2865—2869).—By the action of bromacetophenone on ethyl sodacetoacetate in alcoholic solution, sodium bromide separates, and in a few minutes the reaction is complete:—

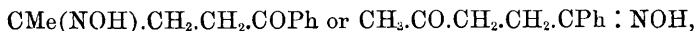


The product is diluted with water, the oil which separates taken up with ether, the solution dried with calcium chloride and evaporated. The heavy, slightly reddish-brown coloured oil obtained (*ethyl acetophenoneacetoacetate*) is almost insoluble in water; it is decomposed by distillation, even under diminished pressure. In order to prepare acetophenoneacetoacetic acid,  $\text{CH}_2\text{Bz.CH}_3\text{Ac.COOH}$ , its ethyl-derivative is treated with rather more than the calculated quantity of a 2 per cent. aqueous potash solution for some hours with repeated agitation; it is then filtered into dilute sulphuric acid, when the liquid at first becomes milky, the liberated acid however soon becoming crystalline. This is extracted with ether, the solution evaporated,

and the crystalline mass washed with ether to remove adhering oil. It is of a pure white, but rapidly becomes yellow, dissolves in alkalis with a yellow colour, and on warming the solution an oil separates; but from a cold solution the acid can be reprecipitated unchanged by mineral acids. It melts at about  $130-140^{\circ}$ , heat decomposing it into carbonic anhydride and an oil. Owing to the readiness with which it is decomposed, this acid has not been obtained pure enough for analysis; after two crystallisations from ether the oil already mentioned alone remains. This oil is *acetophenoneacetone*,



and can be obtained in larger quantities by heating acetophenoneacetic acid with absolute alcohol, when carbonic anhydride is abundantly evolved. Acetophenoneacetone is a yellowish oil, heavier than water, in which it is sparingly soluble in the cold, somewhat more readily when heated; it is insoluble in alkalis. By distillation under diminished pressure, water is given off, an oil of penetrating odour passing over, whilst a portion of the diketone is entirely decomposed. The author has not succeeded in obtaining a di-isonitroso-derivative by means of Meyer's hydroxylamine reaction. The mon-isonitroso-derivative,



is obtained on mixing the calculated quantities of hydroxylamine, diketone, and sodium carbonate in dilute alcoholic solution, when it soon separates in small crystals. It forms long white lustrous needles melting at  $122-123^{\circ}$ , and soluble in acids and in alkali. When ethyl acetophenoneacetoacetate is added to boiling alcoholic potash, the mixture boiled for a short time, poured into water and dilute sulphuric acid added, an acid,  $\text{C}_{12}\text{H}_{10}\text{O}_3$ , is precipitated in yellowish flakes; this crystallises from dilute alcohol in clusters of long needles melting at  $114-115^{\circ}$ . Its formation is explained thus:— $\text{C}_{14}\text{H}_{16}\text{O}_4 + \text{KOH} = \text{C}_{12}\text{H}_9\text{O}_3\text{K} + \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$ .  
A. K. M.

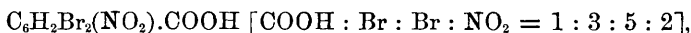
**Substituted Benzoic Acids.** By H. HÜBNER (*Annalen*, **222**, 166—203). Part II.—This paper is a continuation, in conjunction with other investigators, of Part I, already abstracted (this vol., 314).

**V. Metabromometanitrobenzoic Acid and its Derivatives.** By F. HESEMANN and L. KÜCHLER.—Metamidometanitrobenzoic acid is dissolved in glacial acetic acid, aqueous hydrobromic acid (sp. gr. 1.49) added, the cold mixture saturated with nitrous anhydride, and the whole then heated until nitrogen ceases to be evolved. The crude acid is purified by means of its crystalline barium salt. Metabromometanitrobenzoic acid crystallises in needles or plates melting at  $161^{\circ}$ . It is easily soluble in alcohol, ether, and glacial acetic acid, more sparingly in benzene, carbon bisulphide, and chloroform, very sparingly in water. The *potassium salt*,  $\text{C}_7\text{H}_3\text{BrNO}_4\text{K} + \frac{1}{2}\text{H}_2\text{O}$ , crystallises in long, yellowish, glistening needles: the *barium salt*,  $(\text{C}_7\text{H}_3\text{BrNO}_4)_2\text{Ba} + 5\frac{1}{2}\text{H}_2\text{O}$ , in colourless needles easily soluble in boiling, sparingly so in cold water: the *calcium salt*,  $(\text{C}_7\text{H}_3\text{BrNO}_4)_2\text{Ca}$

+  $\text{H}_2\text{O}$ , in colourless prisms: the *magnesium salt* in colourless needles with 1 mol.  $\text{H}_2\text{O}$ : the *zinc salt* in small colourless needles with  $4\frac{1}{2}\text{H}_2\text{O}$ : the *cadmium salt* in colourless needles with  $4\frac{1}{2}\text{H}_2\text{O}$ : the *strontium salt* in colourless anhydrous needles: the anhydrous *silver salt* forms a white precipitate very sparingly soluble in boiling water, from which it crystallises in long colourless needles: the *lead salt* forms a white precipitate.

*Metabromometamidobenzoic acid* was obtained by the reduction of the nitro-acid with tin and hydrochloric acid. It is thus obtained in the form of its hydrochloride, from which the free acid is liberated by sodium acetate. It crystallises in needles melting at  $215^\circ$ , easily soluble in alcohol, sparingly in benzene, almost insoluble in water. The metallic salts crystallise with difficulty; those formed with acids easily. The hydrochloride,  $\text{C}_7\text{H}_6\text{BrNO}_2\cdot\text{HCl}$ , crystallises in prisms easily soluble in boiling water: the sulphate,  $(\text{C}_7\text{H}_6\text{BrNO}_2)_2\cdot\text{H}_2\text{SO}_4$ , in prisms which are decomposed by water. The *barium salt* crystallises with  $4\text{H}_2\text{O}$ ; the *calcium salt* with  $5\frac{1}{2}\text{H}_2\text{O}$ ; the *silver salt* forms an almost insoluble crystalline precipitate. *Dimetabromobenzoic acid* was obtained from the bromamido-acid by means of the diazo-reaction. It is easily soluble in alcohol and glacial acetic acid, sparingly in benzene and boiling water; crystallises in flakes and melts at  $213-214^\circ$ . The *barium salt* crystallises in colourless needles with  $4\text{H}_2\text{O}$ ; the *calcium salt* with  $5\text{H}_2\text{O}$ ; the *cadmium salt* with  $4\text{H}_2\text{O}$ ; and the *lead salt* forms an insoluble white precipitate.

*Dimetabromorthonitrobenzoic acid*,



was obtained by gradually adding the dibromo-acid to about 10 times its weight of warm fuming nitric acid (sp. gr. 1.53). It crystallises in long colourless needles, sparingly soluble in boiling water, benzene, and glacial acetic acid; easily in ether and boiling alcohol. It melts at  $233-234^\circ$ , and sublimes unchanged. The *barium salt* crystallises with  $4\text{H}_2\text{O}$ ; the *potassium* and *calcium salts* yield anhydrous crystals; the *lead* and *silver salts* almost insoluble white precipitates.

*Dimetabromorthamidobenzoic acid*, obtained by the reduction of the nitro-acid with tin and hydrochloric acid, crystallises in colourless needles soluble in glacial acetic acid, hot concentrated hydrochloric acid, and boiling alcohol; almost insoluble in water; it melts at  $225^\circ$ . The *barium* and *calcium salts* crystallise with  $4\text{H}_2\text{O}$ ; the *copper salt* forms a light green crystalline precipitate: the *alkaline salts* crystallise from water with difficulty, more easily from alcohol. The ortho-position of the amido- and nitro-groups in these two acids was proved by the reduction of the amido-acid with sodium-amalgam. The orthamidobenzoic acid, melting at  $143-144^\circ$ , obtained, was converted into salicylic acid by the diazo-reaction.

## VI. Parabromobenzoic and Parachlorobenzoic Acids and their Derivatives.

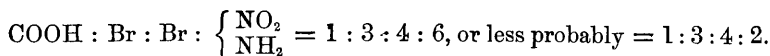
**Parabromometanitrobenzoic Acid.** By J. W. RAVEILL.—This acid, obtained by adding pure parabromobenzoic acid, melting at  $248^\circ$ , to slightly warmed fuming nitric acid, crystallises in long colourless needles easily soluble in alcohol and boiling water, sparingly so in

cold water: it melts at  $199^{\circ}$ . *Parabromometamidobenzoic acid* was prepared by the reduction of the nitro-acid with tin and hydrochloric acid. It forms small colourless needles which become reddish when exposed to the light. It fuses at  $225^{\circ}$  and sublimes unchanged. Burghard has examined the following compounds of this acid. *Parabromometamidobenzoic acid hydrochloride* forms colourless needles which become discoloured by exposure to light; the sulphate,  $(C_7H_6BrNO_2)_2 \cdot H_2SO_4$ , crystallises in needles; the nitrate in flat prisms: all three compounds are decomposed by water. The *copper salt* forms a green, the *lead salt* a white insoluble powder. *Metamidobenzoic acid*, melting at  $174^{\circ}$ , was obtained by the action of sodium-amalgam on the bromo-amido-acid, thus proving the meta-position of the nitro- and amido-groups. *Parachlorometanitrobenzoic acid*, melting at  $179-180^{\circ}$  (Hübner and Biedermann, *Annalen*, **147**, 257), has been re-examined. Its *calcium salt*,  $(C_7H_3ClNO_4)_2Ca + 5\frac{1}{2}H_2O$ , forms yellowish needles which effloresce in the air: the *sodium salt*,  $C_7H_3ClNO_4Na + (?)H_2O$ , crystallises in long yellowish needles easily soluble in water, sparingly in alcohol. The *ethyl salt* was obtained by acting on parachlorometanitrobenzoyl chloride (prepared by treating the acid with phosphoric chloride at  $120^{\circ}$ ) with alcohol. It forms long yellow needles easily soluble in alcohol, benzene, and glacial acetic acid, very sparingly so in water, and melting at  $59^{\circ}$ . *Parachlorometanitrobenzamide* is produced by acting on the benzoyl chloride with aniline. It crystallises in shining prisms, easily soluble in alcohol, benzene, and glacial acetic acid, almost insoluble in water. It melts at  $131^{\circ}$ . By reducing the nitro-acid with tin and hydrochloric acid, it yields the amido-acid, which is further reduced to *metamidobenzoic acid* by the action of sodium-amalgam.

**Parabromometabromobenzoic Acid.** By BURGHARD and BEUT-NAGEL.—This acid was obtained by diazotising parabromometamidobenzoic acid and decomposing the resulting compound with hydrobromic acid. It forms colourless needles or plates, easily soluble in alcohol, sparingly in water, and melts at  $229-230^{\circ}$ . The *barium* and *strontium salts* both crystallise in needles with  $4H_2O$ : the *copper salt* is precipitated from solution as an insoluble light-green powder: the *silver salt* first separates in a gelatinous form, becoming afterwards flocculent: the *lead salt* is pale yellow, the *zinc salt* a white powder: the *potassium salt* forms a very soluble crystalline mass. The *ethylic salt* crystallises from chloroform in long needles melting at  $38-38.5^{\circ}$ . Dibromobenzamide was prepared from the acid chloride by treatment with aniline. It crystallises in small needles melting at  $151.5^{\circ}$ .

**Parametadibromorthonitrobenzoic Acid.** By E. F. SMITH.—Prepared by dissolving the dibromo-acid in fuming nitric acid heated to  $100^{\circ}$ . It is easily soluble in boiling water and in alcohol, crystallises in colourless needles, melts at  $162^{\circ}$ , and sublimes under partial decomposition. The *barium salt* crystallises with 1 mol.  $H_2O$ : the *calcium salt* with  $3\frac{1}{2}H_2O$ : the *sodium* and *potassium salts* give easily soluble, the *magnesium salt* sparingly soluble anhydrous crystals: the *ammonium salt* forms colourless needles: *lead*, *copper*, *iron*, and *silver salts* yield respectively white, green, yellow, and white precipitates. *Parametadibromorthamidobenzoic acid*, obtained by the

reduction of the nitro-acid, is very sparingly soluble in water, more easily in alcohol, from which it crystallises in colourless needles melting at  $225^{\circ}$ . The *barium salt* crystallises with  $4\text{H}_2\text{O}$ ; the *strontium salt* with  $2\text{H}_2\text{O}$ ; the *calcium salt* with  $4\frac{1}{2}\text{H}_2\text{O}$ : *copper salts* yield a yellow precipitate; *lead salts* a white precipitate; and *silver salts* a white precipitate which is decomposed by boiling water: the sodium salt yields very soluble scales. The ortho-position of the nitro- and amido-groups in these acids was proved by M. Ulrich by converting them successively into orthamidobenzoic acid and salicylic acid. Their constitution is therefore—



**VII. Orthochlorobenzoic Acid and its Derivatives.** By F. WILKENS and G. RACK.—*Orthochlorobenzamylide* (Kekulé, *Annalen*, 117, 157) melts at  $114^{\circ}$ . Dissolved in cold fuming nitric acid it yields *orthochlorobenzoparanitranilide*,  $\text{C}_6\text{H}_4\text{Cl.CO.NH.C}_6\text{H}_4\text{NO}_2$ . The latter crystallises in yellow needles soluble in alcohol, benzene, and glacial acetic acid, but insoluble in water, and melts at  $180^{\circ}$ . Heated with alcoholic potash, it yields paranitraniline and orthochlorobenzoic acid. In the process of nitration, a small quantity of the ortho-nitranilide appears always to accompany the para-body. Orthochlorometanitrobenzoic acid was obtained by Hübner (*Ber.*, 6, 175) by adding orthochlorobenzoic acid to about five times its weight of fuming nitric acid and heating gently until the former was dissolved. Rack has carefully investigated this reaction, but could find no trace of an isomeric acid: small quantities of a *chlorodinitrobenzoic acid* crystallising in colourless needles easily soluble in water, alcohol, and ether and petroleum, melting at  $238^{\circ}$ , were however obtained. The *ammonium salt* of orthochlorometanitrobenzoic acid crystallises in easily soluble anhydrous plates; the sodium salt in soluble needles; the *barium salt* in yellow needles with  $3\text{H}_2\text{O}$ ; the *strontium salt* with  $4\frac{1}{2}\text{H}_2\text{O}$ ; the *zinc salt* in long easily soluble needles with  $5\frac{1}{2}\text{H}_2\text{O}$ ; the *cadmium salt* with  $5\text{H}_2\text{O}$ ; the *lead salt* yields anhydrous yellow needles; the copper salt sparingly soluble blue needles. The following new salts of the orthochlorometamidobenzoic acid, obtained by the reduction of the nitro-acid, have been examined:—A dark-green *basic copper salt*,  $(\text{C}_7\text{H}_5\text{ClNO}_2\text{Cu})_2\text{O}$ ; the *lead salt* crystallises in brownish needles with  $1\frac{1}{2}\text{H}_2\text{O}$ ; the *barium salt* could not be obtained in a crystalline form. The *hydrochloride* forms small needles easily soluble in water: the *acid sulphate* forms large colourless needles, and suffers slight decomposition on solution: the nitrate crystallises in reddish easily soluble needles. With sodium-amalgam, this acid yields metamidobenzoic acid. The nitro-group must therefore be in the *meta*-position to the carboxylic-group, and the constitution be  $\text{COOH} : \text{Cl} : \text{NO}_2 = 1 : 2 : 5$  or, less probably  $= 1 : 2 : 3$ .

*Orthochlorometachlorobenzoic acid* was obtained from the chlor-amido-acid by means of the diazo-reaction. It crystallises in colourless needles melting at  $150^{\circ}$ , and is soluble in 1176 parts of water at  $14^{\circ}$ , more soluble in boiling water. The *barium salt* yields efflorescent and easily soluble needles with  $3\text{H}_2\text{O}$ ; the *calcium salt* colourless

needles with  $2\text{H}_2\text{O}$ : the *lead salt* forms a white precipitate. Ortho-metachlorobenzanilide crystallises from benzene in large prisms melting at  $240^\circ$ .  
L. T. T.

**$\beta$ -Phenyltribromopropionic Acid.** By L. P. KINNICUTT and G. M. PALMER (*Amer. Chem. J.*, **5**, 583—587).— $\beta$ -phenyltribromopropionic acid is prepared by the action of dry bromine on  $\beta$ -monobromocinnamic acid; it is crystalline, melts at  $151^\circ$ , and is soluble in alcohol, ether, carbon bisulphide, chloroform, and benzene. (According to Glaser, *Annalen*, **143**, 339,  $\beta$ -bromocinnamic acid melts whilst absorbing bromine, and the liquid acid thus formed solidifies after some days, and then melts at  $45$ — $48^\circ$ . The authors cannot confirm this statement.) When boiled with water,  $\beta$ -phenyltribromopropionic acid yields dibromostyrene,  $\alpha$ -monobromocinnamic acid, and a crystalline acid of the formula  $\text{C}_9\text{H}_5\text{Br}_2\text{O}_3$ , melting at  $184^\circ$ , readily soluble in water, alcohol, and ether, soluble in chloroform, sparingly soluble in carbon bisulphide and benzene; it is probably phenyldibromolactic acid.

Dibromostyrene, on exposure to bromine-vapour, is converted into a thick viscous oil of the formula  $\text{C}_8\text{H}_5\text{Br}_4$ . This is soluble in alcohol, ether, and carbon bisulphide, and is readily decomposed by heat.

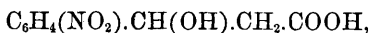
A. J. G.

**Substituted Aromatic  $\beta$ -Lactones and Derivatives of Cinnamic Acid.** By A. BASLER (*Ber.*, **16**, 3001—3007).—This is an account of the para-derivatives of nitrocinnamic acid, the ortho-derivatives of which have been prepared by A. Einhorn (*Abstr.*, 1884, 65). *Paranitrophenyl- $\beta$ -bromopropionic acid*,



is not obtained direct from paranitrocinnamic acid, as is the ortho-acid, but by the action of 5 parts hydrobromic acid dissolved in glacial acetic acid at  $0^\circ$ , on the dry ether, subsequently heating it for two or three hours in a sealed tube at  $100^\circ$ . The acid crystallises out and is purified by recrystallisation from alcohol or acetone. It forms white cubical crystals, melting with decomposition at  $170$ — $172^\circ$ , dissolves in the above-mentioned solvents, but is nearly insoluble in other ordinary solvents, and is decomposed by water. Concentrated sulphuric acid dissolves it in the cold, and decomposes it on heating. Boiled with dilute sulphuric acid (1 to 4), it yields paranitrocinnamic acid by separation of water from intermediately formed paranitrophenyllactic acid. When boiled with water, it yields 27.5 per cent. paranitrostyrene and 72 per cent. paranitrophenyllactic acid. With sodium carbonate in the cold, the reaction is precisely similar to that of the ortho-acid (*Abstr.*, 1884, 65), but with boiling sodium carbonate it yielded 29 per cent. nitrostyrene and 65 per cent. paranitrophenyl- $\beta$  lactic acid. The *ethyl derivative* is very stable, but on prolonged boiling with soda or water yields paranitrocinnamic acid, without any nitrostyrene or the expected nitrophenyllactic acid.

*β-Lactone of paranitrophenyllactic acid*,  $C_6H_4(NO_2).CH<\overset{CH_2}{\underset{-O-}{CO}}$ , is obtained by the action of sodium carbonate in the cold as described by Einhorn for the ortho-compound. It crystallises from absolute alcohol in needles, melting at  $91.9^\circ$ , and is soluble in hot benzene, alcohol, and ether. The following reactions are proof of its being a *β*-lactone:—1st. On heating it slightly above the melting point, it forms paranitrostyrene with evolution of carbonic anhydride. 2nd. With hydrobromic acid in glacial acetic acid, the original acid is regenerated. 3rd. With water or alkali the corresponding or hydroxy-acid is formed, which may be converted into the original acid by treatment with hydrobromic acid at  $150^\circ$ . 4th. The hydroxy-acid,

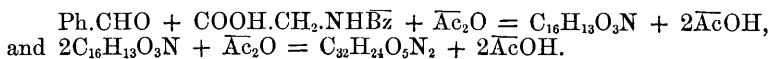


is identical with the oxidation-product of the substance formed by the condensation of paranitrobenzaldehyde and aldehyde, melting at  $129-131^\circ$ .

*Paranitrostyrene*,  $C_6H_4(NO_2).CH:CH_2$ , obtained by heating the lactone, crystallises from hot light petroleum in yellow prisms, melting at  $29^\circ$ , which smell of cinnamic alcohol, and by further application of heat or in time, are converted into a polymeric insoluble form. It is decomposed by distillation.

*Paranitrostyrene dibromide*,  $C_6H_4(NO_2).CHBr.CH_2Br$ , is formed from the above by the action of bromine. It is crystalline, melting at  $72-73^\circ$ , and is soluble in hot benzene, alcohol, and ether. *Paranitrophenyl-β-lactic acid*,  $C_6H_4(NO_2).CH(OH).CH_2.COOH$ , is obtained as mentioned above by heating the lactone with 20 times its volume of water. On evaporation, the acid crystallises out without water of crystallisation, melting at  $130-132^\circ$ , and is barely soluble in cold water, ether, or benzene, but soluble in hot water, alcohol, ether, and light petroleum. Unlike the lactones, it is very stable. With dilute sulphuric acid, it behaves as does the ortho-acid; with calcium and silver, it forms crystalline soluble salts. The *ethyl* and *methyl derivatives* melt at  $45^\circ$  and  $72-74^\circ$  respectively. The action of ammonia, &c., on the *β*-lactones is under investigation. A. B.

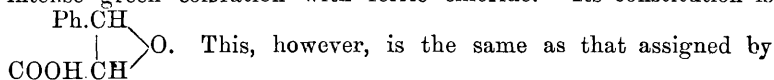
**Phenylglycidic Acid.** By J. PLÖCHL (*Ber.*, **16**, 2815—2825).—When benzaldehyde and hippuric acid are heated with excess of acetic anhydride, a condensation-product is produced, and may be purified by recrystallisation from hot alcohol. It melts at  $164-165^\circ$ , has a feebly alkaline reaction, is insoluble in water, sparingly soluble in ether, more readily in hot alcohol, from which it crystallises in yellow needles. Its formation may be represented thus:



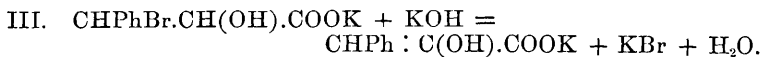
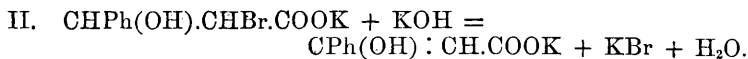
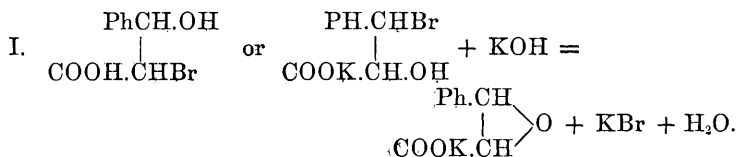
It is the anhydride of benzoylimidocinnamic acid, 
$$\begin{array}{c} PhCH \\ | \\ COOH.CH \end{array} > N\overline{Bz},$$
 into which it may be converted by heating with mineral acids until the yellow colour has disappeared. By saponification with alkalis, a



portion of the acid is decomposed and the yield considerably diminished. Benzoylimidocinnamic acid crystallises in monoclinic needles resembling those of hippuric acid; it melts at  $225^{\circ}$  with decomposition, is almost insoluble in water, readily soluble in ether and alcohol. That this substance has the above constitution and not that of benzoylamidocinnamic acid,  $\text{CHPh}:\text{C}(\text{NHBz})\text{COOH}$ , is indicated by its properties. It yields no addition-compound with hydrobromic acid, and is not converted into a nitroso-derivative by nitrous acid. Heated with dilute hydrochloric acid at  $120^{\circ}$  in a sealed tube, ammonium chloride, benzoic acid, a new acid of the formula  $\text{C}_9\text{H}_8\text{O}_3$ , and a substance (probably a polymeric phenylethylene oxide) insoluble in sodium carbonate solution are formed, the latter crystallising in glistening flat needles melting at  $171^{\circ}$ . The benzoic acid is separated from the oxy-acid by fractional precipitation from the alkaline solution, the acid  $\text{C}_9\text{H}_8\text{O}_3$  being precipitated last as an oil. The same acid is also obtained if benzoylimidocinnamic acid is boiled with alkalis as long as ammonia is evolved. It is a strong acid, very sparingly soluble even in hot water, readily in ether and alcohol, and crystallises from chloroform in lustrous scales melting at  $154\text{--}155^{\circ}$ , with evolution of carbonic anhydride; its alcoholic solution gives an intense green coloration with ferric chloride. Its constitution is



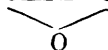
Erlenmeyer to Glaser's phenyloxyacrylic acid (*Annalen*, **147**, 100; *Ber.*, **13**, 300), a body of very different properties to the above. Since epichlorhydrin can be obtained from both dichlorhydrins, and glycidic acid from both  $\alpha$ - and  $\beta$ -chlorolactic acids, the two phenylbromolactic acids might be expected to yield the same phenylglycidic acid, unless in the splitting off of the hydrobromic acid the bromine should combine with the hydrogen-atom directly united to the carbon, in which case hydroxycinnamic acids would be formed.



On treating phenyl- $\beta$ -bromolactic acid with alcoholic potash, the chief product is resinous, but the potassium salts of two acids are also produced, neither of which is identical with Glaser's phenyloxyacrylic acid. The one salt is decomposed by mineral acids, yielding phenyl-ethaldehyde and styrcinic acid, whilst the other yields a stable acid melting at  $154\text{--}155^{\circ}$ , and identical with the author's phenylglycidic

acid. This acid cannot be obtained from phenyl- $\alpha$ -bromolactic acid, either by means of alcoholic or of aqueous alkalis. The experiments show that whilst phenyl- $\beta$ -bromolactic acid is decomposed according to equations I and III (see above), the corresponding  $\alpha$ -acid suffers only the one decomposition shown in equation II. Phenylglycidic acid resembles glycidic acid in yielding an amido-derivative when heated with ammonia at  $100^\circ$ , whilst Glaser's phenoxyacrylic acid yields no amido-acid under like conditions. Phenylamidolactic acid is sparingly soluble in water, insoluble in ether, soluble in hot alcohol, from which it crystallises in prisms melting at  $189$ — $190^\circ$ . Phenylglycidic acid, unlike glycidic acid, does not combine with hydrobromic acid, but this is readily explained by the resistance offered by the very negative character of the compound, the conversion of the stable saturated phenylglycidic acid into the less stable phenyl- $\beta$ -bromolactic acid being improbable. On the assumption of Erlenmeyer's formula for Glaser's phenoxyacrylic acid, this would be expected to yield  $\alpha$ -phenyllactic acid by reduction; the  $\beta$ -acid, melting at  $94^\circ$ , is however produced, whilst the  $\alpha$ -acid is readily obtained by the reduction of the author's phenylglycidic acid.

From these results, it is inferred that Glaser's phenoxyacrylic acid, obtained from phenyl- $\alpha$ -bromolactic acid, is  $\beta$ -hydroxycinnamic acid,  $\text{CPh}(\text{OH}) : \text{CH} \cdot \text{COOH}$ , and that the two acids obtained from phenyl- $\beta$ -bromolactic acid are distinct from Glaser's acid, the one being  $\alpha$ -hydroxycinnamic acid,  $\text{CHPh} : \text{C}(\text{OH}) \cdot \text{COOH}$ , and the other phenylglycidic acid,  $\text{CHPh} - \text{CH} \cdot \text{COOH}$ , with which the author's



oxy-acid (see above) is identical.

With regard to the influence of the phenyl-group, the author points out the stability of the salts of the halogen-lactic acids of the fatty series, those of the two phenyl-halogen-lactic acids being very unstable, although the acids themselves are stable; whilst the former yield the same glycidic acids on treatment with alcoholic potash, those of the aromatic series yield unsaturated hydroxy-acids, and in the case of phenyl- $\beta$ -bromolactic acid also a small quantity of phenylglycidic acid. Both glycidic and phenylglycidic acids are stable, and both yield stable salts.

The above condensation of benzaldehyde and hippuric acid differs from Perkin's reaction, the carbon-atom of the aldehyde radicle uniting with both nitrogen- and carbon-atoms in the hippuric acid.

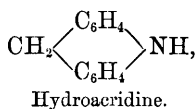
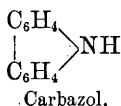
A. K. M.

**Violet Derivatives of Triphenylmethane.** By O. FISCHER and G. KÖRNER (*Ber.*, **16**, 2904—2911).—In continuation of work published by Fisher and German (*Abstr.*, 1883, 1097) the authors of this paper confirm the presence of other substances (containing free amido-hydrogen) in commercial methyl-violet besides the dye which yields the reduction-product melting at  $173^\circ$  (hexamethylparaleucaniline). When methyl-violet prepared from pure dimethylaniline is reduced and the product crystallised from alcohol, the substance melting at  $173^\circ$  separates out, whilst the mother-liquor contains other substances yielding acetyl-derivatives, which show the same behaviour

on oxidation as tetramethylacetylparaleucaniline previously described. The methyl-violet is heated with an excess of acetic anhydride and fused sodium acetate for several hours on a water-bath, the melt dissolved in water and the dye-stuff precipitated by salt and zinc chloride. The substance obtained is dissolved in water and fractionally precipitated by salt, when the unattacked violet separates first, the green acetyl-derivative remaining in solution. On adding alkali to the solution, a grey flocculent precipitate is obtained, which, after recrystallisation from alcohol, melts at 223—225°. The figures obtained on analysis agree with the formula  $C_{26}H_{33}N_3O_3$  (diacetylpentamethylpararosaniline). Investigation shows that one acetyl-group is attached to nitrogen, whilst the other is united to the oxygen of the carbinol-group. It is insoluble in water, sparingly soluble in alcohol, the solution assuming a violet coloration on exposure to air; on adding acetic acid, the formation of the green dye takes place gradually in the cold, instantly on heating. The salts are soluble in water with splendid emerald-green coloration, but the dye is too unstable to be of technical value. On reducing the acetic acid solution with zinc-dust and adding alkali, a precipitate is obtained, crystallising from alcohol in aggregates of colourless concentrically-grouped needles melting at 142—143°, and from the numbers obtained on analysis is very probably *acetylpentamethylparaleucaniline*,  $C_{26}H_{31}N_3O$ . By careful oxidation, it is reconverted into the green dye-stuff. On boiling it with hydrochloric acid, the acetyl-group is split off, and *pentamethylparaleucaniline*,  $C_{24}H_{29}N_3$ , obtained, crystallising from dilute alcohol in groups of colourless needles, melting at 115—116°; on oxidation, it yields a violet intermediate in shade between tetra- and hexa-methyl-violet. The position of the amido-groups is the same as in the tetra- and hexa-methylparaleucaniline and in paraleucaniline, since it yields the same methiodide as the latter when heated at 100° with methyl iodide and methyl alcohol. It is thus shown to be a true methyl-derivative of paraleucaniline. A. K. M.

**Acridine.** By C. GRAEBE (*Ber.*, 16, 2828—2832).—The researches of Riedel (*Abstr.*, 1883, 1152) and of Bernthsen and Bender (*Abstr.*, 1883, 1133) show that the formula of acridine is most probably  $C_{13}H_9N$ , and not  $C_{12}H_9N$ , as previously assumed by Graebe and Caro. The author has prepared the pure base from repeatedly crystallised hydrochloride and sulphite, and on analysing it his figures also agree with the formula  $C_{13}H_9N$ . The low percentage of carbon obtained in previous analyses is probably due to the absorption of oxygen by the acridine, which is especially observable when the latter is melted. Analyses of the platinochloride,  $(C_{13}H_9N)_2 \cdot H_2PtCl_6$ , and aurochloride,  $C_{13}H_9N \cdot HAuCl_4$ , also confirm the above formula, whilst the author's previous vapour-density determination (6.02) agrees well with both formulæ. Acridine sulphite,  $(C_{13}H_9N)_2 \cdot H_2SO_3$ , is obtained as a very characteristic salt by the action of sulphurous acid on a solution of the hydrochloride; it separates in the form of reddish-brown needles. It can also be prepared by mixing solutions of acridine hydrochloride and sodium sulphite, and then acidulating with hydrochloric acid, when it is obtained in larger yellowish-red needles. If, instead of

acidulating, the solution be concentrated, the salt  $C_{13}H_9N, SO_3NaH$  crystallises out in colourless prisms, very soluble in water. On heating its solutions, cridine and acridine sulphite are produced. The addition of hydrochloric acid precipitates acridine sulphite. *Octohydroacridine*,  $C_{13}H_{17}N$ , is prepared by heating acridine (5 grams) or its hydrochloride (6 grams) with amorphous phosphorus (2 grams), and hydriodic acid (6—7 c.c.) for 6—7 hours at  $220-230^\circ$ . The product is crystallised from water and the base separated by means of ammonia. It crystallises from alcohol in colourless scales or long plates, melts at  $84^\circ$ , and distils at  $320^\circ$ . Its solutions do not fluoresce, and it has not the powerful action on the skin and mucous membrane so characteristic of acridine. The hydrochloride,  $C_{13}H_{17}N, HCl$ , forms colourless plates, readily soluble in hot, sparingly in cold water. With acetic anhydride and with benzoic chloride, it yields acetic and benzoic derivatives, and with methyl iodide, it forms methylacetohydroacridine. In the conversion of hydroacridine into octohydroacridine, a well characterised base is produced from a non-basic imido-compound, a change analogous to the conversion of carbazol into carbazoline :



the reduction of the  $C_6H_4$ -groups affecting the chemical character of the nitrogen in the same way in both cases. A. K. M.

**Hydrides of Naphthalene.** By C. GRAEBE and P. A. GUYE (*Ber.*, 16, 3028—3032).—Agrestini (Abstr., 1883, 345) having, in his attempt to prepare Graebe's naphthalene tetrahydride, only obtained naphthalene hexhydride along with naphthalene, the authors repeated the former experiments (this Journal, 1873, 1008). Their results confirm the work previously published. They heated 10 grams of naphthalene, 3 of red phosphorus, and 9 of hydriodic acid boiling at  $127^\circ$  in a sealed tube at  $210-225^\circ$  for  $7\frac{1}{2}$  hours, and obtained without any separation of iodine 7—8 grams naphthalene tetrahydride boiling at  $205^\circ$ . The difference in Agrestini's results seem to be due to the higher temperature ( $235^\circ$ ) which he employed. Analysis and a vapour-pressure estimation confirmed the formula  $C_{10}H_{12}$ , but in a short time the hydride is partially oxidised.

Tetrahydronaphthalenesulphonic acid was also again prepared. The monosulphonic acid is obtained by heating the tetrahydride with  $3\frac{1}{2}$  parts of concentrated sulphuric acid at  $40^\circ$  for three hours. At  $100^\circ$  the disulphonic acid is formed. The sodium salt,  $C_{10}H_{11}SO_3Na$ , is soluble in alcohol and water, and crystallises in plates. The barium salt,  $(C_{10}H_{11}SO_3)_2Ba\frac{1}{2}H_2O$ , is soluble in hot water and alcohol, and crystallises in plates.

Naphthalene hexhydride is obtained by heating 6.7 grams naphthalene with 3 of red phosphorus, and  $9\frac{1}{2}$  of hydriodic acid ( $127^\circ$  b. p.) in a sealed tube for nine hours at  $245^\circ$ . No iodine separates out, but some phosphonium iodide is formed. About 80 per cent. of a hydride

is obtained, which analysis proves to be the hexhydride. Its boiling point is  $199.5^{\circ}$ ; Agrestini gives  $205^{\circ}$ , and the authors suppose that his specimen may have been slightly oxidised, as they have found that by oxidation in air the boiling point of these hydrides is raised. The observation that *naphthalene dihydride* can be obtained by treating naphthalene trihydride with bromine was also confirmed.

## A. B

**Two Isomeric Benzylnaphthalenes.** By C. VINCENT and L. ROUX (*Bull. Soc. Chim.* [2], **40**, 163—166).—A good yield of  $\alpha$ -benzylnaphthalene is obtained by heating a mixture of benzyl chloride and naphthalene at  $150^{\circ}$  for  $1\frac{1}{2}$  hours, zinc chloride being added from time to time in small quantities. The product is decanted before it solidifies in order to remove the zinc chloride; it is then purified by distillation and by recrystallisation from alcohol. After drying over sulphuric acid, it is crumbled to powder between the fingers and sifted. The  $\alpha$ -derivative passes through the meshes, and is purified by two or three crystallisations from alcohol. The  $\beta$ -derivative is retained by the sieve.

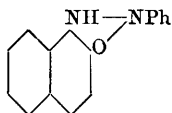
Pure  $\alpha$ -benzylnaphthalene is deposited from alcohol in brilliant rhombic plates, which act powerfully on polarised light. The crystals (sp. gr. 1.165) dissolve freely in benzene, chloroform, ether, and boiling alcohol. They melt at  $59^{\circ}$ , and boil at  $345^{\circ}$ .

The  $\beta$ -compound is best prepared by heating a mixture of benzyl chloride and naphthalene at  $160^{\circ}$  for an hour, aluminium chloride being added in small quantities. The product is poured into water, and then distilled and purified by recrystallisation from boiling alcohol. The crystals melt at  $55^{\circ}$ , and boil at  $315^{\circ}$ . Their sp. gr. at  $0^{\circ}$  is 1.176. The compound is freely soluble in benzene, chloroform, and boiling alcohol.

By the prolonged action of nitric acid,  $\alpha$ -benzylnaphthalene is converted into  $\alpha$ -naphthyl phenyl ketone melting at  $75^{\circ}$ , and the  $\beta$ -compound into the  $\beta$ -ketone, which melts at  $81.5^{\circ}$ . W. C. W.

**Constitution of Azonaphthol-dyes.** By C. LIEBERMANN (*Ber.*, **16**, 2858—2864).—From an observation made by Pfaff, the author is led to an opinion opposed to that generally accepted that the two series of azo-derivatives obtained from  $\alpha$ - and  $\beta$ -naphthol respectively are alike constituted, except in the difference of positions of the  $\alpha$ - and  $\beta$ -hydroxyl groups. When the calculated quantity of aniline hydrochloride and sodium nitrite is added to  $\alpha$ -naphthol in a thin paste, the formation of the dye-stuff begins at once; whilst, if the same mode of proceeding be adopted with  $\beta$ -naphthol, the mixture remains practically colourless, the dye being, however, produced on the addition of alkali. Similar results are obtained when other aromatic bases are substituted for aniline. A more striking difference between the  $\alpha$ - and  $\beta$ -derivatives is the ready solubility of the  $\alpha$ -compound,  $\text{Ph.N}_2\text{C}_{10}\text{H}_7\text{OH}$ , even in cold dilute alkali; whilst the corresponding  $\beta$ -compound is quite insoluble in cold alkali, dissolves slightly on heating, and separates unchanged when the solution cools. The  $\beta$ -dye-stuffs are also distinguished from the corresponding  $\alpha$ -compounds by their capacity for crystallising, their more sparing solubility, and

their lower melting points. *Benzene-azo- $\alpha$ -naphthol*,  $\text{Ph.N}_2.\text{C}_{10}\text{H}_8.\text{OH}$ , prepared as above, and recrystallised from alcohol, forms steel-blue needles melting at  $193^\circ$ , with evolution of gas. According to Typke (*Ber.*, **10**, 1580), who employed a different method of preparation, two isomerides exist melting at  $166^\circ$  and  $175^\circ$  respectively. The author has not yet succeeded in establishing the existence of an isomeride. *Benzene-azo- $\beta$ -naphthol*,  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}$ , separates from boiling alcohol in lustrous golden-red coloured scales when the solution is rapidly cooled, and when slowly cooled, in long needles of a cantharides-like lustre. It forms a rosaniline-red solution with concentrated sulphuric acid, and is also soluble in ether, benzene, light petroleum, and carbon bisulphide. It melts at  $134^\circ$ , is insoluble in aqueous alkali, but is readily dissolved even by cold sodium ethylate, from which solution water reprecipitates it unchanged. It has feebly basic properties, uniting with hydrochloric and hydrobromic acids to form unstable compounds. *Benzene-azo- $\alpha$ -naphthol* also dissolves in these acids, but to a very small extent. On reduction, *benzene-azo- $\beta$ -naphthol* yields  $\alpha$ -amido- $\beta$ -naphthol and aniline, showing that the diazo-group occupies the ortho-position to the hydroxyl in the naphthalene nucleus. This ortho-grouping is one however which, as shown by Jacobsen and Liebermann, also by Worms and by Böttcher (*Abstr.*, 1883, 1113), readily yields anhydro-compounds. The application of this view to *benzene-azo- $\beta$ -naphthol* leads to the constitution



which at once explains the insolubility of this compound in alkali, and also the lower melting points of the  $\beta$ -derivatives. The same explanation will also probably hold for the very numerous sulphonated azonaphthol-dyes employed in the arts. Anthrol, which, from the position of the hydroxyl-group, may be compared with  $\beta$ -naphthol, also yields azo-derivatives, insoluble in alkali. The less ready formation of the  $\beta$ -naphtholazo-dyes is explained by the fact of there being no para-position for the azo-group to assume, which is therefore forced to take up the ortho-position.

A. K. M.

**Reactions of Hydroxylamine.** By E. NÄGELI (*Ber.*, **16**, 2981—2984).—*Derivatives of Camphoroxime* (*Abstr.*, 1883, 728).—Camphoroxime with dry hydrochloric acid yields camphoroxime hydrochloride,  $\text{C}_{10}\text{H}_{16}:\text{N.OH.HCl}$ . It is a white powder, insoluble in ether, sparingly soluble in water, but readily in alcohol and acids. With sodium ethylate, it gives the sodium salt,  $\text{C}_{10}\text{H}_{16}:\text{N.ONa}$ , and with sodium ethylate and ethyl iodide ethylcamphoroxime,  $\text{C}_{10}\text{H}_{16}:\text{N.OEt}$ . No acetyl-compound is formed with acetic chloride, but a liquid anhydride boiling at  $216\text{--}218^\circ$  of the formula  $\text{C}_9\text{H}_{15}:\text{C}:\text{N}$ .

As hydroxylamine reacts with amylene oxide obtained by boiling

amylene bromide with water, the author was led to doubt that the group  $\text{O} \begin{array}{c} \diagup \text{C} \\ | \\ \diagdown \text{C} \end{array}$  could exist in the oxide as Niederist (*Annalen*, **196**, 360)

had supposed, more especially as Meyer had observed that hydroxylamine does not react with ethylene oxide, or generally with substances containing that group; and as Eltekoff (*Jour. Russ. Chem. Soc.*, **10**, 215) had obtained methyl isopropyl ketone by boiling amylene bromide with water and oxide of lead. The author found that on preparing methyl isopropyl ketone, and treating it with hydroxylamine, he obtained a compound identical with that obtained from amylene oxide. Both boiled at 157—158°, had the same odour and all the reactions of acetoximes. Analysis gives the formula of methylisopropylacetoxime,  $\text{CHMe}_2\text{CMe}:\text{NOH}$ . There seems little doubt, therefore, that Niederist's supposed amylene oxide is methyl isopropyl ketone, as shown by the equation  $\text{CHMe}_2\text{CHBr}\cdot\text{CH}_2\text{Br} + \text{H}_2\text{O} = 2\text{HBr} + \text{CHMe}_2\text{COMe}$ .  
A. B.

**Matico-camphor.** By K. KÜGLER (*Ber.*, **16**, 2841—2843).—A specimen of matico-camphor (from *Piper angustifolium*), examined by the author had the odour and taste of matico-leaves, and melted between 89° and 103°. After repeated crystallisations, it melted at 94°, the mother-liquors containing a yellow amorphous resin. Matico-camphor exhibits a rotatory motion on the surface of water; it is not attacked by aqueous alkalis, is readily soluble in alcohol, ether, chloroform, benzene, and light petroleum. The pure substance lacks both taste and odour. In contact with hydrochloric acid, it assumes an intense violet colour, which changes to blue and then to green, the compound yielding brown crystals from ether, showing green fluorescence, and having an ethereal odour. With sulphuric acid, it becomes yellow, then red, and finally violet. With sulphur and nitric acids, it assumes first a yellow, then a violet, and finally a blue colour. Matico-camphor has the formula  $\text{C}_{12}\text{H}_{20}\text{O}$ ; it is, perhaps, the ethyl-derivative of ordinary camphor.  
A. K. M.

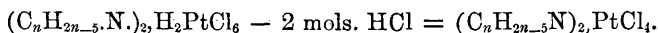
**Pyridine Bases from Coal-tar.** By H. GOLDSCHMIDT and E. J. CONSTAM (*Ber.*, **16**, 2976—2981).—The authors are investigating these bases in order to observe which of the theoretically possible picolines, lutidines, &c., are present in coal-tar. The bases were obtained in the usual way from the tarry acid liquor produced by washing crude benzene with sulphuric acid, by neutralising and subsequently distilling off the volatile bases by steam. From 10 litres of the acid liquor 1 kilo. of volatile bases boiling between 92—200° was obtained. By repeated fractional distillation little was obtained under 100°; about half was pyridine (114—117°), but above 160° very little was obtained. The small fraction under 100° consisted chiefly of a liquid boiling at 92—93°, which had a strong odour of pyridine, and yielded that base after treatment with solid potash and distillation. By mixing pyridine with one-half its volume of water, and distilling, two fractions are obtained, the heavier at 92—93°, the lighter at 115°. The former appears on analysis to be a molecular

compound of water and pyridine ( $C_5H_5N + 3H_2O$ ), judging from the constant boiling point and from its sp. gr. being higher than that of a mixture of water and pyridine.

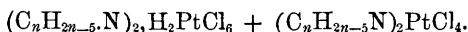
The fraction between  $130^\circ$  and  $140^\circ$  was found to consist of picoline, which on oxidation and treatment with cupric acetate yielded (1) a precipitate of cupric picolate, from which picolinic acid melting at  $137^\circ$  was obtained, thus showing that the picoline in coal-tar is  $\alpha$ -picoline; and (2) a solution of a small quantity of a copper salt, which yielded an acid melting at  $310^\circ$ , giving on analysis the formula of a pyridinemonomonocarboxylic acid. This is isonicotinic acid or  $\gamma$ -pyridine-carboxylic acid, and is derived possibly from  $\gamma$ -picoline present in the coal-tar, but more likely from the oxidation of some lutidine present as an impurity, which Weidel and Herzig (*Vienna Acad. Ber.*, 1880, 848) have shown does yield isonicotinic acid. The presence of  $\alpha$ -picoline was also verified by a careful preparation, an analysis, and a crystallographical examination of the platinochloride.

A. B.

**Anderson's Reaction.** By O. DE CONINCK (*Bull. Soc. Chim.* [2], 40, 271—276 and 466).—When the platinochloride of a pyridine base is treated with boiling water, 2 mols. HCl are eliminated, and the new salt combines with the unaltered platinochloride to form a double salt, e.g.,



The double salt has the composition



The author points out that this reaction, which he terms "Anderson's Reaction," is characteristic of pyridine bases. It distinguishes between pyridine and quinoline platinochlorides, as the latter are not affected by boiling water. The hydroquinoline platinochlorides are, however, easily decomposed. The platinochloride of quinoline, derived from cinchonine, and that of quinoline prepared synthetically, both resist the action of boiling water to precisely the same extent. The author therefore regards these bases as identical. The exact conditions for the formation of the double salt are difficult to attain. If the action of the boiling water on the platinochloride is not continued for a sufficient length of time, the double salt is mixed with unaltered platinochloride. If it is carried on too far, then it is partly decomposed.

W. C. W.

**Action of Pyridine Bases on Alcoholic Iodides.** By O. DE CONINCK (*Bull. Soc. Chim.* [2], 40, 276—279).—Methyl iodide unites rapidly with pyridine bases. Ethyl iodide enters into combination less rapidly, and by means of this reagent, it is possible to distinguish between three classes of pyridine bases:—1. Cinchonine and brucine combine energetically with ethyl iodide. 2. Coal-tar pyridine bases unite less readily. 3. Dippel-oil bases combine slowly with ethyl iodide. Pyridine combines more rapidly than picoline, and  $\beta$ -collidine more rapidly than  $\beta$ -lutidine. Skraup's quinoline prepared by



synthesis, and quinoline from cinchonine, require the same time for their union with ethyl iodide. W. C. W.

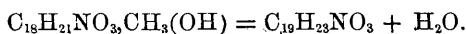
**Creatines and Creatinines.** By E. DUVILLIER (*Compt. rend.*, **97**, 1486—1487. See also Abstr., 1883, 220 and 1153).—If a saturated aqueous solution of cyanamide is mixed with an equivalent quantity of ethylamido- $\alpha$ -butyric acid and a few drops of ammonia, the liquid after about a month begins to deposit bulky tabular crystals of dicyandiamide, and dicyandiamide and ethylamido- $\alpha$ -butyrocyamidine remain in solution. Ethylamido- $\alpha$ -butyrocyamidine,  $C_7H_{13}N_3O$ , forms somewhat large transparent anhydrous tabular crystals which are very soluble in water and alcohol.

The action of cyanamide on ethylamido-isovaleric acid did not yield satisfactory results. C. H. B.

**Morphine.** By O. HESSE (*Annalen*, **222**, 203—234).—The author has studied the action of acetic and propionic anhydrides on morphine and its derivatives. With regard to the nomenclature introduced by Grimaux, the author contends that the term codeïne is unjustifiable. When the hydroxylic hydrogen in morphine is replaced by the acetyl group, the resulting product is mono- (or di-) *acetylmorphine*; and when it is similarly replaced by methyl, &c., the resulting compounds should be called *methylmorphine*, &c., and not codeïne, codethyline, &c. For derivatives where one of the hydrogen-atoms of the nucleus is replaced by methyl, &c., the author proposes the name of *morphimethine*, &c.

Morphine dissolves easily in excess of acetic anhydride at  $85^\circ$ , to form *diacetylmorphine*. This substance crystallises in anhydrous prisms, which are easily soluble in alcohol, sparingly so in ether, melt at  $169^\circ$ , and with hydrochloric acid yield a hydrochloride which gives no coloration with ferric chloride. No more highly acetylated body could be obtained. *Dipropionylmorphine* was prepared in a similar manner. It is amorphous, easily soluble in alcohol, ether, and chloroform, sparingly so in water. The *hydrochloride* is an amorphous powder easily soluble in water and yielding a pale yellow amorphous *platinochloride*,  $[C_{17}H_{17}(C_3H_5O)_2NO_3]_2, H_2PtCl_6$ . Morphine methiodide treated with freshly precipitated silver chloride yields *morphine methochloride* crystallising in long colourless needles, containing  $2H_2O$ , which it loses at  $120^\circ$ . It dissolves in concentrated sulphuric acid without discoloration, but the solution turns violet when heated. It gives a dark blue coloration with ferric chloride in aqueous solution. The *platinochloride* forms orange needles containing 1 mol.  $H_2O$ . Morphine methiodide dissolves with difficulty in acetic anhydride at  $100$ — $120^\circ$ , and forms the diacetyl-compound. The yield is, however, very bad, a much more satisfactory result being obtained with morphine methochloride. *Diacetylmorphine methochloride* crystallises in concentrically grouped needles, which are easily soluble in water, and give no coloration with ferric chloride. From its solutions potassium iodide precipitates *diacetylmorphine methiodide*. The chloride yields a pale yellow *platinochloride* crystallising in small needles containing 1 mol.  $H_2O$ , which they partly lose on exposure to the air, com-

pletely at 110°. The action of methyl iodide on morphine in the presence of bases has already been studied by Grimaux (Abstr., 1881, 829). With acetic anhydride codeine (methyilmorphine) gives *acetylcodeine* crystallising from ether in prisms which melt at 133°. When propionic is substituted for acetic anhydride, *propionylcodeine* (*propionylmethyilmorphine*) is formed; on evaporating its ethereal solution, this is left as a colourless film easily soluble in ether, benzene, and alcohol. It dissolves in sulphuric acid with a bluish tint, which turns dark blue on the addition of a trace of ferric chloride. When heated, both solutions turn dark green. It yields crystallisable salts with acids. The *hydrochloride* crystallises in large colourless needles containing 2H<sub>2</sub>O, and soluble in water and alcohol: it gives a yellow crystalline *platinochloride*. The *acetate* crystallises in colourless needles soluble in water. It loses a part of its acetic acid at 100°. The *hydriodide* crystallising with 1 mol. H<sub>2</sub>O, the *oxalate* with 3H<sub>2</sub>O, and the sulphate are all soluble in water. *Codeine methochloride* (*methyilmorphine methochloride*) is obtained from codeine methiodide by treatment with silver chloride; and crystallises in large rhombic prisms with 1 mol. H<sub>2</sub>O. It yields a yellow flocculent *platinochloride* with 3H<sub>2</sub>O. The *sulphate* gives colourless needles containing 4H<sub>2</sub>O. A solution of the last-named salt yields, with barium hydroxide, a colourless solution of *codeine methylhydroxide*, which on evaporation over sulphuric acid, deposits crystals of *methocodeine* (*methyilmorphine methine*). The unchanged hydroxide solution precipitates hydrates from solutions of metallic salts, and rapidly absorbs carbonic anhydride from the air. Codeine methiodide dissolves in acetic anhydride at 85°, and deposits oblong rectangular tables of *acetylcodeine methiodide* on cooling. Thus obtained, the crystals are anhydrous; but on recrystallisation from alcohol, colourless needles containing 4H<sub>2</sub>O are obtained. The *platinochloride* forms a yellow crystalline precipitate. If a solution of sodium, potassium, ammonium, barium, or calcium hydroxide be added to an aqueous solution of codeine methiodide, a colourless strongly alkaline solution is obtained which gradually becomes coloured, and deposits *methocodeine*. The reaction is quickened by using an excess of the alkali and heating to boiling. The action of the alkalis is therefore to liberate the hydroxide from which the elements of water are subsequently eliminated,



For the preparation on a large scale, it is best to boil the methiodide with rather more than the molecular weight of potassium hydroxide, extract the hot solution with benzene, and shake out the latter with acetic acid. The acetic solution is then saturated with sodium chloride, and the precipitated chloride recrystallised from a small quantity of water. A concentrated aqueous solution of the chloride is then decomposed with sodium hydroxide, and the base at once extracted with ether. In a few minutes the ethereal solution deposits long colourless prisms of methocodeine. Freshly precipitated, this substance dissolves freely in ether, but when crystallised only sparingly. It crystallises from boiling alcohol in prisms, from boiling water in needles, in the latter case with 1 mol. H<sub>2</sub>O. It melts at 118.5°, and

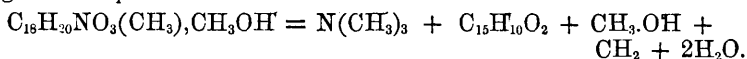
dissolved in 97 per cent. alcohol gives  $[\alpha]_D = -208.6^\circ$  when  $p = 4$  and  $t = 15^\circ$ . In moderately concentrated sulphuric acid, the base and its salts dissolve to a colourless solution, which gradually becomes of a purplish-violet tint, and turns olive-green when heated. The base gives a blue colour when heated with concentrated sulphuric acid. The *hydrochloride* crystallises with  $2\text{H}_2\text{O}$  in needles soluble in 10.8 parts of water at  $18^\circ$ . The *platinochloride* is of a dark green colour.

Methocodeine dissolves in acetic anhydride at  $85^\circ$ , and yields *acetylmethocodeine*. It melts at  $66^\circ$ , and gives a blue coloration with concentrated sulphuric acid. It is soluble in alcohol, sparingly so in water. The salts crystallise easily: the *hydrochloride* with  $\frac{1}{2}\text{H}_2\text{O}$ , the *platinochloride* with  $4\text{H}_2\text{O}$ , the nitrate with  $3\text{H}_2\text{O}$ , and the sulphate with  $8\text{H}_2\text{O}$ .

With methyl iodide, methocodeine forms  *$\alpha$ -methocodeine methiodide*, crystallising in prisms with  $\frac{1}{2}\text{H}_2\text{O}$  and soluble in water. The  *$\alpha$ -methochloride* is obtained from the methiodide by the action of silver chloride, but could not be obtained in a crystalline form. It gives a blue colour with concentrated sulphuric acid. The  *$\alpha$ -platinochloride* is a yellow flocculent precipitate.  *$\alpha$ -Codeine methochloride* dissolves in acetic anhydride forming  *$\alpha$ -acetylcodeine methochloride*, which crystallises with  $2\frac{1}{2}\text{H}_2\text{O}$  in long colourless silky needles, easily soluble in alcohol and boiling water, sparingly so in cold water. It gives up 2 mols.  $\text{H}_2\text{O}$  at  $100^\circ$ , but the remainder cannot be expelled without decomposition setting in. With concentrated sulphuric acid it gives a brownish-red coloration. The *platinochloride* forms a sparingly soluble yellow crystalline precipitate. An aqueous solution of the  *$\alpha$ -iodide* becomes milky on addition of potassium or sodium hydroxide, and gradually deposits an oil which appears to be unchanged iodide. If, however, the solution be boiled with alkali, an oil is deposited on cooling, which solidifies after a time. This substance is not the original iodide, but is isomeric with it, and the author therefore names it  *$\beta$ -codeine methiodide*. It differs from the  *$\alpha$ -iodide* in crystalline form, in containing no water of crystallisation, and in being less soluble in water. The  *$\beta$ -chloride* was not obtained in the crystalline form, and gave a purplish-violet colour with concentrated sulphuric acid. The  *$\beta$ -platinochloride* yields small orange needles: the sulphate is amorphous. Decomposed with barium hydroxide, the sulphate yields the alkaline  *$\beta$ -methocodeine methylhydroxide*, which crystallises in small colourless plates and flat prisms, soluble in water and alcohol. If the solution be evaporated at  $30\text{--}40^\circ$ , an amorphous deliquescent and highly caustic mass is left. This, however, is not a pure body. The  *$\beta$ -chloride* yields  *$\beta$ -acetyl-methocodeine methochloride*, from which the  *$\beta$ -iodide* can be obtained by double decomposition. The *platinochloride* forms a yellow powder containing  $3\text{H}_2\text{O}$ .

These results confirm the presence of only two hydroxyl-groups in morphine; and the author points out that these two groups are different in character, the hydrogen of one being replaceable by either positive or negative radicals, that of the other only by the radicals of the fatty acids. Morphine methiodide is not decomposed by boiling

with bases, whereas directly the hydroxylic hydrogen-atom is replaced by an alcohol radical, the stability of the methiodide is at once reduced, and in the presence of bases, its decomposition and the introduction of the methyl radical into the nucleus takes place even at ordinary temperatures. The author believes the hydrogen-atom thus replaced to be one in close proximity to the hydroxyl-group which is only displaceable by acid radicals, and not, as Gerichten and Schrötter contend, one of those combined with the nitrogen-atom. He declines to accept as proved, the formation of methylethylpropylamine by the decomposition of ethocodeïne methyl-hydroxide, on which Gerichten and Schrötter base their argument. On the latter supposition, the author should have obtained dimethylpropylamine by the decomposition of methocodeïne methyl-hydroxide, whereas he only obtained trimethylamine. He believes the decomposition to take place according to the equation—



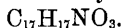
The ethyl compound would then give ethylene in the place of methylene, and this was observed by Gerichten and Schrötter, but ascribed by them to a secondary reaction.

The author is inclined to look upon *laudanine* as a morphine derivative containing propionyl, but in which the relative character and stability of the two hydroxyl-groups is different to what is the case in morphine. He is now continuing his researches in that direction.

L. T. T.

**Pseudomorphine.** By O. HESSE (*Annalen*, **222**, 234—248).—In his first communication on this alkaloïd, which he obtained from opium, the author stated his belief that it was identical with the oxymorphine of Schützenberger, and that its formula was:  $\text{C}_{17}\text{H}_{19}\text{NO}_4$ . Brockmann and Polstorff (*Abstr.*, 1880, 408) contended that this oxymorphine had the constitution  $(\text{C}_{17}\text{H}_{18}\text{NO}_3)_2$ , and based their assumption principally on the fact that nitric oxide was evolved in its production from a solution of morphine hydrochloride and silver nitrite, whereas the formula  $\text{C}_{17}\text{H}_{19}\text{NO}_4$  would require an evolution of nitrous oxide. The author now shows that if an aqueous solution of morphine hydrochloride is mixed in molecular proportions with a solution of potassium nitrite, and the whole heated for some time at  $60^\circ$ , crystals of oxymorphine are formed, and a gas evolved which does not turn red in contact with the air, and is consequently not nitric oxide. The formation is evidently due to the decomposition of morphine nitrite,  $2\text{C}_{17}\text{H}_{19}\text{NO}_3, \text{HNO}_2 = 2\text{C}_{17}\text{H}_{19}\text{NO}_4 + \text{N}_2\text{O} + \text{H}_2\text{O}$ , and the author points out that an evolution of nitric oxide, when silver nitrite is used, might also be explained by the equation  $4\text{C}_{17}\text{H}_{19}\text{NO}_3, \text{HNO}_3 = 4\text{C}_{17}\text{H}_{19}\text{NO}_4 + \text{N}_2 + \text{N}_2\text{O}_2 + 2\text{H}_2\text{O}$ .

The author now finds that the body  $\text{C}_{17}\text{H}_{19}\text{NO}_4$  is a hydrate of the real base, and that the formula for oxymorphine is therefore



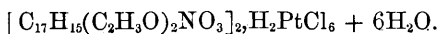
The hydrate loses its water at  $130^\circ$ , but the base is so very hygroscopic that it is only by taking special precautions that rehydration can be prevented. The less crystalline the specimen in question, the more

marked is its hygroscopic character. The alkaloïd is best purified by solution in ammonia, from which it crystallises in colourless crusts containing  $1\frac{1}{2}\text{H}_2\text{O}$ , which it loses at  $130^\circ$ . The *hydrochloride*,  $\text{C}_{17}\text{H}_{17}\text{NO}_3\cdot\text{HCl}$ , crystallises in scales containing, under varying conditions, respectively 1, 2, 3, and 4 mols.  $\text{H}_2\text{O}$ . A *basic hydrochloride*,  $(\text{C}_{17}\text{H}_{17}\text{NO}_3)_2\cdot\text{HCl} + 6\text{H}_2\text{O}$ , is obtained in microscopic crystals from a hot neutral acetic solution on the addition of sodium chloride: from a cold solution, the basic salt crystallises with  $8\text{H}_2\text{O}$ . With platinum chloride both the neutral and basic salts yield a yellow flocculent platinochloride,  $(\text{C}_{17}\text{H}_{17}\text{NO}_3)_2\cdot\text{H}_2\text{PtCl}_6$ .

The *hydriodide*,  $\text{C}_{17}\text{H}_{17}\text{NO}_3\cdot\text{HI} + \text{H}_2\text{O}$ , loses its water when exposed to the air: the *chromate*,  $(\text{C}_{17}\text{H}_{17}\text{NO}_3)_2\cdot\text{H}_2\text{Cr}_2\text{O}_7 + 6\text{H}_2\text{O}$ , loses  $4\text{H}_2\text{O}$  at  $80^\circ$ : the sulphate crystallises with  $6\text{H}_2\text{O}$ , and effloresces slightly in dry air, but when crystallised from boiling water it is stable: the *oxalate* yields shining scales, with  $8\text{H}_2\text{O}$ : the *acid tartrate*,



crystallises in needles or prisms. Heated for two hours at  $120^\circ$  with acetic anhydride, pseudomorphine yields *diacetyl pseudomorphine*,  $\text{C}_{17}\text{H}_{15}(\text{C}_2\text{H}_3\text{O}_2)_2\text{NO}_3$ . It crystallises from ether in concentrically grouped flat prisms, containing  $4\text{H}_2\text{O}$ , which it loses in the desiccator. It is moderately soluble in ether and chloroform, very soluble in alcohol, in which it yields a strongly alkaline solution. It contracts at  $250^\circ$ , but does not melt until  $276^\circ$ . It gives no coloration with ferric chloride. With hydrochloric acid, it forms a salt crystallising in quadratic tables, easily soluble in water. With platinum chloride, this salt yields a pale yellow flocculent *platinochloride*,



The di-acetyl compound is easily reconverted into the original base by heating it with alcoholic potash. It is clear, therefore, that the hydroxyl-groups of morphine are still present in pseudomorphine. The author was unable to obtain a methyl compound by the action of potassium hydroxide and methyl iodide. He, however, obtained pseudomorphine methyl-hydroxide,  $\text{C}_{17}\text{H}_{17}\text{NO}_3\cdot\text{MeOH}$ . The author also believes pseudomorphine to be identical with the substance which E. L. Meyer (*Ber.*, 4, 121) obtained by the action of moderately concentrated sulphuric acid on a nitro-compound which he had obtained by passing a strong current of nitrous anhydride into water in which morphine was suspended.

L. T. T.

**Ptomaines and Analogous Compounds.** By A. G. POUCHET (*Compt. rend.*, 97, 1560—1562).—The alkaloidal compounds which exist normally in urine, fæces, and the excrements generally, are identical with or very closely related to those formed by the putrefaction of proteids out of contact with air. The alkaloidal products from both sources are certainly mixtures, probably of homologous compounds. They are separated by converting them into tannates, which are then decomposed by lead hydroxide in presence of strong alcohol, the lead being finally removed by hydrogen sulphide, and the liquid submitted to dialysis. After some time, the mixture is separated into

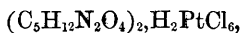
(1) a liquid portion difficult to dialyse, and (2) crystalline substances which dialyse easily.

The liquid portion obtained from urine, which the author terms the *extractive matter of urine*, is a neutral syrupy liquid which does not crystallise even after prolonged exposure in a vacuum. It has the composition  $C_3H_5NO_2$ , yields precipitates with the general reagents for alkaloïds, is altered on exposure to air, is converted into a resin by hydrochloric acid, and is rapidly oxidised when mixed with platinum chloride solution. It does not yield a platinochloride.

The dialysate from urine contains a base  $C_7H_{12}N_4O_2$  or  $C_7H_{14}N_4O_2$ , which crystallises in bundles or irregular spheres, and is soluble in dilute alcohol, almost insoluble in strong alcohol, insoluble in ether. It has a feebly alkaline reaction, and yields crystallisable salts. The platinochloride forms deliquescent golden-yellow rhombic prisms.

The liquid portion from the products of putrefaction is a mixture of volatile bases (probably the hydropyridic bases described by Gautier and Etard) and variable substances.

The dialysate when mixed with platinum chloride yields two platinochlorides, the one,  $(C_7H_{18}N_2O_6)_2, H_2PtCl_6$ , crystallising in prismatic needles, and insoluble in strong alcohol, the other,



forming a dull yellow powder somewhat soluble in strong alcohol, but insoluble in ether. Both these bases are allied to the oxybetaines. Their hydrochlorides form silky needles, which are altered by excess of hydrochloric acid and by exposure to air. The base,  $C_7H_{18}N_2O_6$ , forms short, thick prisms, which become brown when exposed to light, the other,  $C_5H_{12}N_2O_4$ , crystallises in needles which seem to be more stable. Their solutions give the general reactions for alkaloïds. The precipitates with sodium phosphomolybdate are reduced somewhat rapidly, and are soluble in ammonia with formation of a blue solution, like the precipitate formed by aconitine under the same conditions.

All these compounds are violently poisonous to frogs, producing torpor and paralysis, with destruction of reflex action, and rapid death.

C. H. B.

**"Ptomaine."** By J. GUARESCHI and A. MOSSO (*J. pr. Chem.* [2], 28, 504—512).—*Influence of Ptomaine Hydrochloride on Nerves and Muscles.*—The experiments made on frogs after destroying the spinal cord yielded the following results:—When a frog has been poisoned with ptomaine hydrochloride, the gastrocnemius muscle no longer contracts regularly when the ischiadic nerve is slightly irritated. Its irritability is soon lost. It appears as if some time were required for the energy to accumulate in the nerve centre before the same amount of irritation will produce the contraction of the muscle. The authors state that the destruction of the irritability of the motor nerves is by no means an action characteristic of curare, for they find that when a nerve dies from any cause whatever the motive fibres are first affected, and the direct irritability of the muscle is the last to disappear. There is no poison known which kills the muscle and

leaves the nerves their functions. By slightly compressing the ischiadic nerve of a frog with a pair of nippers, the leg becomes paralysed, and exactly the same appearances are manifested during its loss of irritability as are shown in a case of poisoning by curare.

The authors have made a chemical examination of fresh brain substance according to the Stas-Otto method, and find it to contain ammonia, trimethylamine, and ptomaines. The experiment was made in winter, and 24 hours after the death of the animal. An examination was also made of the constituents of fresh beef. Ten minutes after the death of a calf 50 kilos. of its flesh was cut up and heated for several hours on a water-bath with dilute sulphuric acid. The mass then filtered, and the filtrate, after separation of the fat, evaporated to a syrup. This was twice treated with three times its volume of 97 per cent. alcohol. The alcoholic liquor was partially distilled, the volatile products being passed into hydrochloric acid. The remainder was evaporated and the residue treated with ether. On evaporating the ether a yellow residue A was obtained. The acid solution was rendered alkaline by adding ammonia and then shaken with ether. The ether on evaporation left a residue B. Finally the pulpy residue was extracted with benzene. Residue A contained succinic acid, lactic acid, and small quantities of alkaloids. B consisted of a yellow alkaline liquid, which, on standing, deposited microscopic crystals. The quantity obtained was not sufficiently large to allow a thorough analysis to be made. The authors give a list of the reactions of the substance. The residue from benzene consisted of minute traces of alkaloids.

Considering the possibility that in the method just described the alkaloids may be produced by the action of sulphuric acid on the albuminoid substances, the authors repeated the process, substituting tartaric for sulphuric acid. They found that residue A was very much less; succinic acid could not be detected. Residue B was reddish-brown and contained traces of alkaloids.

By extracting the flesh with water only at 50–60°, crystals of methylhydantoin melting at 159–160.5° were obtained, but no trace of alkaloids. It appears that in the absence of foreign acids, fresh acid animal substance yields only traces of alkaloids, or none, and that their formation is due to the decomposition of albuminoid substances.

J. I. W.

**Gelatin.** By H. WEISKE (*Bied. Centr.*, 1883, 673).—The author has prepared gelatin in various ways, and has found that the products differ in properties. Pieces of bone were treated repeatedly and for a long time with dilute hydrochloric acid to remove the inorganic matter as completely as possible; they were then washed. Gelatin made from this is not precipitated from its solutions by tannic acid unless a few drops of a solution of a salt (sodium chloride, &c.) are added simultaneously; in other respects it does not differ from ordinary gelatin. By boiling bones free from mineral matter with repeated quantities of water, and then dissolving the residue by heating with water under pressure, two solutions are obtained which when evaporated to dryness at 100° yield two kinds of gelatin

differing from one another and also from the above variety in various properties.

D. A. L.

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## Physiological Chemistry.

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**Influence of the Salts of Sea-water on Fresh-water Animals and the Causes of the Death of Freshwater Animals in Sea-water and Marine Animals in Fresh Water.** By H. DE VARIGNY and P. BERT (*Bied. Centr.*, 1883, 652—655).—Varigny has studied the influence of some of the salts contained in sea-water on the development of frog-spawn and tadpoles. Their development was not arrested either by solutions containing per litre 2.2 grams magnesium sulphate, or by solutions containing as much as 3 grams of potassium chloride per litre, or even 4 grams of magnesium chloride. Sea-water contains 2.2 grams  $\text{MgSO}_4$ , 0.7 gram  $\text{KCl}$ , 3.5 grams  $\text{MgCl}_2$ , and 20—25 grams  $\text{NaCl}$  per litre. Moreover tadpoles hatched in the 2.2 grams per litre magnesium sulphate solution can thrive in a solution in which the magnesium sulphate is gradually increased to 4 grams per litre. But sodium chloride, even in quantities below the proportion in sea-water, destroys the vitality of frog-spawn and tadpoles. In solutions of equal parts of fresh and sea-water, tadpoles 10—20 days old die, whilst those 5 or 6 weeks old make scarcely any perceptible progress in their development. These results confirm those obtained by Bert (*Compt. rend.*, 97, 133), who, moreover, points out that the amount of chlorides in sea-water is sufficient to kill fresh-water animals in from 30—40 minutes. The cause of death in animals protected by slime is exosmotic action on the gills; whilst in animals not so protected, such as frogs, &c., the body becomes dry through exosmose, and the animal loses from  $\frac{1}{4}$  to  $\frac{1}{3}$  of its weight; thus a frog will die if one of its feet is immersed in sea-water. A fully grown and uninjured eel can live a long time in sea-water; if, however, any of the protecting slime is removed the animal dies in a few hours. Larger animals can resist this action better than smaller ones. The activity of the water increases as the temperature rises. Experiments were now made on adaptability, and it was observed that when sea-water is gradually added to fresh water containing living tadpoles, crustaceans, &c. (also conferva), the animals (and plants) continue to live in a salted fresh water in which they would soon succumb if removed direct from fresh water into such a mixture. Perfect adaptation was obtained with the crustacean water-fleas, for after some time they became so accustomed to the mixed waters that they died when they were returned to their original element—fresh water. In another experiment with these animals 1 part of sea-water was added to 2 parts of fresh water; within a few days all the animals died, but in another few days fresh animals appeared, having been hatched from the eggs of their deceased progenitors, from which they differed only in size.

Fresh water infusoria and conferva can withstand a water contain-

ing enough salt to kill fish and crustaceans, which is about the quantity equivalent to a mixture of 1 part sea with 2 parts fresh water. They may be made to live in a water equivalent to equal parts of sea and fresh water, provided the amount of salt is only increased at the rate of 0.1 gram per litre per diem.

By converse experiments with marine animals the authors find that they die in fresh water from want of sodium chloride; and the want cannot be supplied by either potassium or magnesium salts, or by raising the sp. gr. of the fresh water by means of glycerol or sugar, &c.

The immediate cause of death is endosmosis; the gills of fish, mollusca and annelida swell, whilst the muscles of annelida and amphioxus and the arms of cephalopoda lose their power of contraction.

Adaptation experiments with marine animals under reverse conditions to those described above, give perfectly analogous results. The authors are now studying the effect on marine animals of raising the quantity of salt in sea-water.

D. A. L.

**Influence of Fresh Water on Marine Animals and Vice Versâ.** By F. PLATEAU (*Bied. Centr.*, 1883, 786).—The author was working in this direction in 1870, and arrived at the same results as Varigny and P. Bert (preceding Abstract), in spite of the fact that his method was a totally different one.

J. K. C.

**Action of Cold and Warm Baths on the Temperature of the Animal Body.** By A. PLETZER (*Bied. Centr.*, 1883, 712).—It is a known fact that cold baths lower the temperature of the body, but that in consequence of the external cooling the influence of the regulating power of the skin is soon at work, and causes an increase in temperature. If, however, an animal cooled by cold water is immersed in a warm bath a further reduction of temperature takes place with astonishing rapidity. This fact has been verified by many experiments with healthy and feverish rabbits; the following are examples of the investigations:—

*Temperature of Animal at Starting, 38.6—38.7° C.*

Temperature of bath, °C.....	30	40	9
„ „ animal, °C... ..	38.5—38.2	38.1—38.0	38.05
Temperature of bath, °C.....	40	9	40
„ „ animal, °C... ..	37.7—37.5	37.5	37.0—36.8

*Feverish Animal, 40.2—40.3° C.*

Temperature of bath, °C.....	30	40	29	12	40
Temperature of animal, °C... ..	40.0	39.8—39.7	39.7—39.4	(air) 39.0	38.6—38.5
Temperature of bath, °C. ....	9	40	9	40	
„ „ animal, °C. ..	38.3	37.8—37.2	37.5	36.6	

In one case the temperature of the body was reduced  $5^{\circ}$  by alternate treatment with warm and cold water. It was also observed that simultaneously with the lowering of the temperature there is a decrease in the amount of oxygen required, and consequently a reduction in the oxidation-process of the body.

D. A. L.

**Comparative Value of Fresh and Artificial Butter.** By A. MAYER and P. ULDALL (*Bied. Centr.*, 1883, 776—778).—This paper gives the results of Mayer's work (which has already been abstracted in this Journal, Abstr., 1884, 92), together with some critical remarks by Uldall. The latter adverts to a feature in Mayer's experiments, that the persons under treatment were not fed for some days previously with the butter on trial. This, however, he thinks would only slightly alter the results in favour of artificial butter, making the digestibility of the two about equal.

J. K. C.

**Value of Bran for Human Food.** By M. RUBNER (*Bied. Centr.*, 1882, 677—679).—Bran, as is well known, contains nearly the same proportion of the most important group of food constituents as flour, the quantity of albuminoids and fat being even greater; therefore the question as to the expediency of employing flour prepared from the entire grain, or flour without bran, for bread-making is a very important one, and of course amounts to this:—Is it better to separate the bran and use it as fodder for cattle, or to leave it in the flour employed for human food? In order to decide this point, the author has conducted some experiments which, along with his conclusions, are briefly described below. A man was fed on bread made from different qualities of flour; he received about 900 grams of bread and 1.5 litre of beer daily, water being given if more drink was required. The experiments were continued for periods of three days. The qualities of flour employed were:—1. The *finest* constituting 30 per cent. of the yield from wheat-corn, which was a mixture of Odessa, Californian, and English wheat. 2. A *medium quality*, being 70 per cent. of the flour obtained from a mixture of Girka and Minnesota wheat. 3. The *whole-meal flour* of the Bread Reform League. The loss per cent. of the food-constituents passing away unused with the excrement in each case is as follows:—

Kind of flour.	Dry matter.	Nitrogen.	Fat (ether extract).	Carbo-hydrates.	Ash.
Finest . . . . .	4.03	20.07	44.69	1.10	19.28
Medium . . . .	6.66	24.56	62.83	2.57	30.35
Whole meal..	12.23	30.47	51.14	7.37	44.98

These numbers speak for themselves. The cellulose walls of the husk-cells form doubtless the chief obstacle to the complete utilisation of the nutritious matter in coarse bread. The author points out that although the quantity of coarse bread digested in the human body is less than that of fine bread, nevertheless there is a quantity of nutritious matter utilised in the intestines from it and from the bran contained in it; and from this stand-point alone no objection can be

raised against its use as an article of human diet. When however it is used it should be ground very much finer than it is at present customary to do. But from an economical point of view, the use of bran in bread is not recommended, for to obtain it, it is taken from animals which can digest it more completely than human beings, and do therefore obtain more value from it. It is further shown that taking into consideration the husks which must be removed, and other losses which occur during grinding, a greater yield than 85 per cent. cannot in any case be expected from the mill. D. A. L.

**Influence of Feeding with Cotton-cake Meal on Milk Excretion.** (*Bied. Centr.*, 1883, 683—684).—On the whole, results from three series of experiments determine in favour of the use of cotton-cake meal for increasing the yield of milk. D. A. L.

**Guanine in Fish.** By E. EWALD and C. F. W. KRUCKENBERG (*Chem. Centr.*, 1883, 705).—Guanine is pretty generally distributed in the skin of fishes; it is, however, not a characteristic excretion, but is simply produced in certain tissues. D. A. L.

**Researches on the Diseases of Animals.** By PASTEUR and others (*Bied. Centr.*, 1883, 674—677).—Pasteur's results may be summarised as follows:—It is proved by inoculation experiments that both quiet and raving madness originate from the same poison. The symptoms of madness are extremely variable, and depend apparently on the part of the nervous system attacked by the poison. The infectious matter is in the form of microbes in the saliva of mad animals; inoculation with it causes death in three ways—either by microbating the saliva, or by the excessive production of pus, or by the development of madness. The marrow, brain, and spinal cord are always virulent in all animals dying of madness, the virulence increasing until putrefaction sets in. In one case a brain was sustained at a temperature of 12° for three weeks by this action. To produce madness quickly and surely, after trepanning, inoculate in the skin on the surface of the brain; the disease will make its appearance in 6, 8, or 10 days. The malady produced by injection into the blood system exhibits symptoms which differ greatly from those of raving madness caused by a bite or by inoculation after trepanning, and hence many cases of the quiet form may escape observation. In those which may be termed moderate, pronounced paralysis ensues, whilst raving and howling are not observed. When the poison is injected into the blood, the spinal cord seems to be the first point attacked. Injection of saliva or blood from a mad subject into the veins does not protect a dog from a subsequent outbreak of madness or from death after a second inoculation of mad matter, either by trepanning or injection in a vein. Cases of spontaneous recovery have been observed when early symptoms only were developed, but never after the symptoms became violent. In some cases after they had disappeared they returned after two months, whereupon death followed.

As a great many sheep are lost after protective inoculation for sheep-pock, Peuch has investigated the subject, and from the results

of his experiments draws the conclusion that this danger may be greatly reduced by using small quantities of lymph diluted 60—120 times.

Thiernesse and Degive have made experiments on protective inoculation for lung epidemics. Their results show that 2 grams of lung-epidemic poison may be injected into the veins without danger, provided it does not touch the cell-tissue. Immunity to the same extent results from this injection as from the tail inoculation recommended by Willems. Immunity in this case is sometimes perfect, and does not cause changes which occur when the disease is taken in the natural way.

D. A. L.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Effect of Artificial Influences on the Internal Causes of Growth.** By E. WOLLNY (*Bied. Centr.*, 1883, 690—698).—It has been stated that the development of plants can be usefully modified by artificial means (C. Kraus, *ibid.*, 1882, 324). The author has now experimentally proved such to be the case.

*Effect of Drying the Seed Tubers on the Yield of Potatoes.*—The drying was conducted in two ways, either at a moderate room temperature, 8—10°, when the tubers were laid out and exposed to light for some time before sowing, or at 30—35° a short time before planting. In the first case shoots were developed, whereas in the second case no germination ensued. In field experiments, plots planted with seed tubers dried by either method yielded greater weight, larger number, and more large tubers than plots planted with fresh seed tubers at the same time and treated in the same manner as the foregoing. This increase was more marked in the case of plants from small seeds; this result is, however, exceptional. These facts only apply to wet soils and damp climates.

*Influences of Climate, of Condition, and Extent of Soil on the Stem Production of Cultivated Plants.*—Light favours development of side shoots; want of light, on the other hand, favours growth of the stalk; therefore plants grown in diffused light or under the shade of trees do not excel in side shoots. The soil must contain sufficient water, and must be sufficiently warm to supply the necessary nourishment for the development and growth of the side shoots. Thick planting is not recommended, because the plants shade one another, and in this way affect the light, and the growth above ground is excessively long, which is not favourable to side growth. Moreover evaporation is increased, and the temperature and humidity of the soil are therefore lowered, which is detrimental. In fact the stem production is weaker the closer the plants are placed together, other conditions being similar.

*Effect of Mowing and Feeding-off Plants on the Production of Side Shoots.*—Removing the principal stems from plants either by mowing or feeding-off is very beneficial to the reproductive powers of the plants, inasmuch as it reduces the amount of leaf evaporation, and thus increases the amount of water in the soil; this increase is, however, only slight, because at the same time it (mowing, &c.) raises the temperature of the soil by favouring insolation; it also allows the free access of light to the young shoots. It is therefore advisable to cut grasses, clover, &c., as early as possible, for by prolonging the growth the soil becomes dry and the light is shut out from young shoots. Cutting must not be too frequent, for frequent interruption of growth lowers the yield. Even when the ground is already dry it is better to mow the plants, because in case rain comes the leaves of unmown plants hold back the water which would be useful in the soil. Mowing potato plants in an early stage of growth lowered both weight and number of harvested potatoes.

*Removing the shoots from the seed tubers* increases the number of potatoes harvested; there are, however, a smaller number of large and medium tubers, and the total harvest is slightly lowered.

*Removing the top joint* at a not too early period from peas, beans, and vetch plants increased the number of side shoots, but lowered the yield of seed and partly of the straw. Experiments with maize plants, in which the male blossom was removed from alternate plants, so that the blossoms of the untouched plants were sufficient to fertilise all the female blossoms, showed that this operation increased the number of heads, the total harvest, the quantity of ripe corn, and in most cases the straw, whilst the number of shoots from the parent stem was in most cases diminished.

D. A. L.

**Effect of Variations in the Quantity of Oxygen on the Growth of Plants.** By A. WIELER (*Bied. Centr.*, 1883, 715).—The object of the present investigation is to ascertain what reduction of oxygen in the atmosphere is required to arrest vegetable growth, or to diminish the rate of development. Seedlings of the following plants were employed:—*Helianthus annuus*, *Vicia Faba*, *Lupinus luteus*, *Brassica Napus*, *Curcubita Pepo*, *Coprinus lagopus*, *Mucor Mucedo*, and *Phycomyces nitens*. The first experiments showed that the quantity of oxygen capable of sustaining vegetable growth is an extremely small quantity; thus the limit for *L. luteus* is from 1.32 to 0.0001865 c.c.\* of oxygen in 1500 c.c., whilst the limit for *Phycomyces* is from 1.94 to 2.90 c.c. In another series of experiments, plants grown in rarefied air are compared with those grown in atmospheric air. With *H. annuus* growth gradually increases during the diminution of pressure to 100 mm., the growth then diminishes suddenly until 5 to 10 mm. is reached, when the rate of growth is the same as in ordinary air. The maximum of vigour for *V. faba* lies between 100 and 300 mm., whilst the diminution commences at 50 mm. Under increased pressure the growth at first decreases, but subsequently increases, and then becomes more considerable than in

\* This number is very probably a misprint.

the open air. These results help to explain the rapid growth of plants in elevated regions. D. A. L.

**Influence of Radiant Heat on the Growing Parts of Plants.**

By J. WORTMANN (*Bied. Centr.*, 1883, 685—687).—For every species of plant there is a certain range of temperature especially favourable to the growth of the part of the plant exposed to it, and between the maximum and minimum of this range is the most favourable point (the optimum). Experiment has proved that plant-growth depends essentially on the degree of temperature to which a plant is exposed. Van Tieghem has therefore suggested that if the growing part of a plant is exposed to unequal temperatures on different sides, the side exposed to the most favourable temperature would grow quicker than the other, and thus cause curvature with the convexity towards the most favourable source of heat. The author has experimented in this direction with *Phycomyces nitens*, *Lepidium sativum*, and *Zea Mays*, and finds that his observations do not agree with the above hypothesis, inasmuch as the parts of plants capable of curvature bend sometimes towards and sometimes from the source of heat, irrespective of increased or retarded growth resulting from either favourable or unfavourable heating; thus maize always bends towards the source of heat, even when the other side is exposed to the optimum temperature. D. A. L.

**Correlative Growths in the Vegetable Kingdom.**

By J. V. SACHS (*Bied. Centr.*, 1883, 714).—The author applies the term "correlation of growth" to the influence a growing organ exerts on the growth of another organ in the same plant. Many illustrations are given. For example, cutting off the leaf-shoots of a potato plant prevents the formation of underground tubers, whilst removing the underground tubers causes the formation of tubers on the leaf stem above ground. When the radiating top of *Abies excelsa* is removed, lateral branches develop, become vertical, and finally assume the form of radiating tops. This the author explains by the assumption that the organs of the plant act as competitors for the common store of nutritious matter, each homogeneous organ, so to speak, competing for its own special food, its removal, therefore, necessitating a more vigorous attack on the nutritious matter in order to effect its regeneration. Another form of correlation depends on the interdependence of different organs, that is, when the increased or diminished development of an organ influences the development of another organ connected with it functionally as a whole. For instance, in ordinary land plants the development of leaf surface is accompanied by production of chlorophyll, rising of sap, and consequently formation of wood and extension of roots, whilst in submerged water plants capable of absorbing nutriment with their entire surface transpiration is not required, and so the formation of wood and extension of root are found wanting. Other examples are given. D. A. L.

**Influence of the Amount of Soil on the Development of Roots of Various Plants.** By HELLRIEGEL (*Bied. Centr.*, 1883,



756—775).—The proper structure of the roots was first observed by planting seeds in boxes full of sawdust. After growing for six or eight weeks the plants were removed, the roots washed, and their form noted. In the case of the pea, the original tap root throws out branches which grow faster than the tap root, and in time surpass it in length and abundance of secondary roots. Beans begin in the same manner, but the first side roots are stronger and stiffer than those of the pea, and do not grow to such a length. They increase, however, regularly throughout, giving the whole root the form of an inverted cone, the original tap root being the longest. The root of the lupine is developed on an entirely different plan, assuming in time the form of an upright cone, the upper part of the tap root being free from branches, which are almost confined to the lower half. During the earlier stages of growth the roots of all three grow very rapidly, but their relative growth diminishes with the age of the plant. In the case of oats, the total length of root branches was found to average 40 metres per plant. Diminution of the volume of the soil was found to damage lupines earliest, then buckwheat, peas, barley, clover, and beans in descending order. When the quantity of soil is too small for the proper growth of the roots, the crops are damaged in proportion to the diminution in the soil. The same result occurs when the plants are sown too closely together—they do not thrive so well, and their time of vegetation is shorter. In the case of barley, the author found that one plant per kilo. of soil was about the right proportion. The depth at which the seeds were planted (2—6 cm.) made very little difference in the growth of the roots. J. K. C.

**Effect of Altitude on Plant Growth.** By A. ANGOT (*Bied. Centr.*, 1883, 713).—The author has observed that the harvest period of winter rye in France is delayed four days for every increase of 100 meters in altitude. D. A. L.

**Studies on Evaporation.** By A. SORAUER (*Bied. Centr.*, 1883, 687—699; comp. Abstr., 1881, 1059).—Previous researches have shown that the water which is evaporated consists both of that produced within the plant by oxidation and that which has served simply as a carrier of nutritious matter and has passed through the organism undecomposed. It has also been proved that the greater the amount of new substance added, the more carbonic anhydride and water is given up by the plant. Hence, in the author's opinion, the amount of evaporation should indicate the amount of work done by a plant, and vary therefore according to the size of the working parts of the plant. Making use of the data supplied in this manner, the author now finds that with plants of the same species, and grown under like conditions, those having less leaf-surface work harder to produce a definite amount of substance than those having a greater leaf surface, and therefore the transpiration per square centimeter of leaf is smaller the greater the available leaf surface of the individual plant. Thus in some experiments with three gourd plants he found that diminishing the leaf surface by removal of leaves from one plant on two occasions did not alter the amount of evaporation in the least,

and even when half the leaves were removed from another plant, a reduction in the amount of evaporation ensued at first, but after eleven days the evaporation was equal to that of an untouched plant. Thus by removing some of the leaves of a plant, the remaining leaves do relatively more work and develop a higher relative evaporation coefficient than those of an untouched plant. This extra activity is derived from the roots, and therefore the growth above ground is going on at the expense of the subterranean growth, and the result of this diminished root growth is made evident in subsequent development of the plant, *e.g.*, in the size of the organs above ground, &c.

D. A. L.

**Respiration and Transpiration of Fungi.** By G. BONNIER and L. MANGIN (*Bied. Centr.*, 1883, 712).—All the present experiments with fungi prove that the volume of oxygen absorbed during respiration is greater than the volume of carbonic anhydride produced, and in various kinds of fungi the proportion of the absorbed oxygen to the volume of carbonic anhydride fluctuated between 0.55 and 0.81. When the respiration takes place in a confined volume of air, the oxygen is soon entirely consumed, whilst on account of internal respiration large quantities of carbonic anhydride are continually evolved. Respiration increases regularly with the temperature, while the proportion of oxygen to carbonic anhydride does not change perceptibly for one and the same species. The intensity of respiration increases with the humidity of the air. Diffused light, on the other hand, lowers it, the reduction in many cases amounting to two-thirds of the total quantity of carbonic anhydride. Respiration is, however, greater under the influence of the more refrangible rays than it is under the influence of the less refrangible rays.

Evaporation is greater in diffused light than in darkness, the difference amounting in some cases to one-half of the weight of the water evaporated.

D. A. L.

**Function of Tannin in Plants.** By E. KUTSCHER (*Bied. Centr.*, 1883, 713).—Investigations were made with *Vicia faba*, *Helianthus tuberosus* and *annuus*, *Ricinus sanguineus*, and *Phaseolus multiflorus*, plants well adapted for the purpose, as they were found to be typical examples of the different locations of tannin; inasmuch as it is distributed throughout the plant in the *Vicia* and *Helianthus*, whilst it is only local and inactive in the *Ricinus* and *Phaseolus* plants. In the last two species, tannin is not found in the top of the plants, nor in the cell-walls, nor in the general sap during the period of vegetation; moreover, it is never equally distributed throughout the tissue-complex, but is confined in separate secluded cells where it, at the most, changes to a red colouring matter without being used in the general development, whilst with the *Vicia* and *Helianthus* tannin is found in all the tissues soon after germination, but disappears with the formation of organs. *Vicia* tannin is iron-green, *Ricinus* iron-blue. Tannin apparently takes part in the formation of and primary differentiation of the tissues, but does not take part in the further growth of the cell-walls; the most feasible use attributed to this substance is in aiding respiration.

D. A. L.

**Effect of Drying on the Germination of Seeds.** By P. v. TIEGHEM and G. BONNIER (*Bied. Centr.*, 1883, 715).—It is well known that dried seeds can germinate in a perfectly normal manner, and that in such cases the temperature and length of exposure are of the utmost importance. For example, two lots of *Vicia faba* seed were exposed respectively for 24 hours to temperatures of 35° and 85°; both lots were now treated in the same manner, and after three days the 35° lot had germinated, whilst the other lot had not. After eight days, all had germinated; those from the seed exposed to the lower temperature were stronger, and continued developing; whilst those of the 85° portion soon stopped in their germination. Cereal seeds were now dried until they had a constant weight at 100° (*a*) and at 35° (*b*); of series (*a*) none germinated; series (*b*) germinated as follows:—Rye, 100 per cent.; oats, 90; barley, 83; and maize 20 per cent. Rye-grain, even after exposure for a short time to 100°, showed signs of vitality, and after its *drying* (for six days) at 80° and then setting for germination, in four days all the grains had sprouted. The deadly temperature for rye-grain is therefore considerably higher than the coagulating temperature of albumin.

D. A. L.

**Presence of Mannitol in the Anana.** By L. LINDET (*Bull. Soc. Chim.*, 40, 65—66).—In the course of the analysis of ananas from Pernambuco and Brazil, the author isolated crystals of mannitol; the quantity obtained was equal to more than 1 per cent. of the fresh fruit. The identity of the crystals with mannitol was established by combustion, crystalline form, solubility, and absence of rotatory and cupric oxide reducing power.

V. H. V.

**Sulphuring of Vines.** By A. BASAROW (*Bied. Centr.*, 1883, 700).—The author is not satisfied with the explanations already offered as to the manner in which sulphur acts on the vines. He therefore made the air from a sulphured vine pass through a solution of caustic soda, and on subsequent examination he detected sulphurous acid, and determined it in the soda-solution, showing that oxidation of the sulphur takes place.

D. A. L.

**Nature of Hop Mildew and Means of Counteracting it.** By A. SCHWARTZ (*Bied. Centr.*, 1883, 718—719).—Mildew is the result of an unsound state of the hop-plant caused by climatic influences, cold winds, severe frosts, sudden changes of temperature, and excessive humidity, whereby the plant is weakened, its growth hindered, and it therefore becomes an easy prey to the insects. The hop louse, *Phrodon humili*, lays its eggs either in the ground in the neighbourhood of hop gardens or on the stems and leaf-stalks of hop-plants, choosing by preference the sickly plants as noted above. Plants sheltered by trees or hills, or otherwise protected from the changes of weather, are exempt from these visitations. Proximity to the sea is destructive, to a certain extent, to these insects. In wet seasons, plants grown on rich soils are more subject to mildew than those produced on poor and therefore drier soils. Moreover, plants set late can resist the attack better than those sown earlier, inasmuch as

they are less frequently exposed to fluctuations of temperature. Mildew can be prevented by washing with soft soap and water, provided the washing is commenced in time, regularly and systematically continued until the cleansing is complete, and carefully watched.

Further researches are required to study the habits, &c., of these and other leaf lice.

D. A. L.

**Composition of Saxon Barley.** By M. MÄRCKER (*Bied. Centr.*, 1883, 698—700).—The author has compared the results obtained from the examination of several samples of Saxon barley with results obtained from other kinds of barley, in the following manner:—

Constituent.	Mean of results, per cent.		
	For Saxony barley. By the Author.	For the composition of barley.	
		By J. Kahn.	By E. Wolff.
Moisture.....	15·0	13·8	14·3
Albuminoïds.....	8·4	11·2	10·0
Fat .....	1·6	2·1	2·5
Non-nitrogenous extractive matter ..	66·8	65·8	63·9
Fibre.....	4·6	5·2	7·1
Ash .....	3·6	2·2	2·2

It will be observed that in the Saxon barley the percentage of albuminoïds and fibre is low, whilst the amount of non-nitrogenous extractive matter is large; and it is these qualities which make the barley of such high value. With regard to the low percentage of albuminoïds, the author makes no notes of manuring, mode of cultivation, or kinds of barley analysed; if the greater part analysed consisted of Chevalier barley, then the results would necessarily be low, for this variety of barley only contains on an average 8·19 per cent. of albuminoïds.

D. A. L.

**Feeding-stuffs.** By A. VOELCKER (*Bied. Centr.*, 1883, 711).—The author has obtained the following results in various analyses:—

	Locust beans.		Dari seeds.	Millet.		Fine Russian linseed cake.
	Shell and seed.	Seed.		Crushed.	Not crushed.	
Moisture.....	14·73	14·11	12·55	12·85	13·19	11·13
Fat .....	0·62	2·03	2·93	3·91	3·83	10·73
Nitrogenous matter..	5·62	16·94	10·31	11·25	9·56	36·62
Woody fibre.....	5·27	8·81	1·63	7·73	12·51	7·91
Extractive matter ....	30·99	54·50	70·43	60·25	57·06	28·22
Ash .....	2·76	3·61	2·15	4·01	3·85	5·39
Sugar .....	40·01	—	—	—	—	—

The shells of the locust-bean form a condiment; they must not be given in too large a quantity on account of their very sweet taste and poorness in nitrogenous matter. Locust-beans (corn) are very hard, but swell up in water; when ground they constitute an easily digestible and nutritious food. Dari seeds (a kind of sorghum) and millet on account of their comparative poorness in nitrogen are suitable for mixing with highly nitrogenous foods for feeding purposes. Green rye ensilage had the following composition:—

	Moisture.	Lactic acid.	Nitrogenous matter.	Extractive matter.	Woody fibre.	Ash.
Per cent. . .	72.50	0.80	1.99 (0.31 N)	12.86	9.72	2.13

Sheep and cattle ate it readily, and cows gave milk abundantly after eating it. D. A. L.

**Palm-cake and Palm-meal.** By HOLDEFLEISS (*Bied. Centr.*, 1883, 709).—The first of these substances is the residue after pressing out the oil; the second is left after the chemical extraction of the oil. Analysis of these substances yielded the following results per cent.:—

	Moisture.	Albuminoïds.	Fat.	Extractive matter free from nitrogen.	Woody fibre.	Ash.
Cake.	10.69	16.66	7.43	44.76	16.96	3.50
Meal.	12.48	16.66	2.72	40.53	22.79	4.82

D. A. L.

**Amount of Fat and Albuminoïds in Feeding-stuffs.** By P. WAGNER (*Bied. Centr.*, 1883, 710).—161 samples of palm-cake were analysed with the result that—

	6	7	39	32	16 p. c. of samples
contain less than	8	8—9	9—12	12—15	over 15 p. c. of fat;

of 87 samples of rice-meal 17 per cent. contained 10 per cent. of fat; 38, 10—12; 22, 12—14; 23, over 14; whilst 18 per cent. of the samples contained 10 per cent. of albuminoïds; 46, 10—12; and 36, 12 to 14.

Out of 49 samples of decorticated earth-nut cake 31 per cent. contained 9 per cent. of fat; 24, 9 to 11; and 45 over 11; and of albuminoïds 39, 44 per cent.; 35, 44 to 46; 26 over 46. Undecorticated earth-nut, mean of 2, 8.4 per cent. fat; 37.23 per cent. albuminoïds. Wheat-bran, 24 samples. Of fat, 8 contained 3.5; 54, 3.0 to 4.5; 38 over 4.5 per cent.; whilst of albuminoïds 42 per cent. contained 13 per cent.; 50, 13 to 15; 8, 8 to 15 per cent. The mean of six analyses of rape-cake is as follows:—10.71 per cent. fat, 28.73 per cent. albuminoïds, whilst with cotton-cake the mean of six analyses gives 13.7 per cent. fat, 30.90 per cent. albuminoïds: sesame-cake 17.45 per cent. of fat; 31.59 per cent. albuminoïds. D. A. L.

**Old Sugar-beet Seeds as Cattle Food.** By SIMON LEGRAND (*Bied. Centr.*, 1883, 709).—Old and sterile sugar-beet seeds were

ground and mixed with diffusion residue to a homogeneous mass; 3 kilos. of this meal a day per head were given to fattening bullocks as a supplementary food, whilst another lot of cattle had instead 3 kilos. of linseed-cake daily per head. The beet-seed meal was always eaten with great relish, and both lots of animals were in equally good condition.

D. A. L.

**Forests as a Protection against Hailstorms.** By L. GLASER (*Bied. Centr.*, 1883, 723—725).—This is a selection of short reports from various neighbourhoods in Germany, Switzerland, and Italy, showing that hailstorms do not occur in the vicinity of pine forests. Instances are given of localities which when well wooded were absolutely free from hailstorms, but having been stripped of their forests are now often subject to such visitations.

J. K. C.

**Different Soils Rich in Humus and their Behaviour with Water.** By A. EMMERLING and G. LOGES (*Bied. Centr.*, 1883, 655—657).—Three soils have been examined. 1. Heath-turf from dry "grey" sand-soil. 2. Beech humus also from dry "grey" sand-soil. 3. Heath-turf from the wet Jlow moor; they contained respectively 39·73, 33·24, and 75·40 per cent. of moisture, and the air-dried substances yielded the following numbers on analysis:—

		1.	2.	3.
Per cent. ....	Water .....	3·25	1·75	11·56
" .....	Inorganic matter .....	67·58	83·39	8·47
" .....	Humus .....	29·17	14·86	79·97
" .....	Nitrogen .....	0·39	0·53	1·11
In 100,000 parts of	Phosphoric acid .....	45·20	35·80	75·30
air-dried substance, {	Potash .....	32·10	38·60	34·90
soluble in cold 12 per {	Lime .....	88·70	34·70	115·00
cent. hydrochloric {	Magnesia .....	30·40	24·40	181·10
acid .....	Sulphuric acid .....	41·90	19·00	287·80

1500 grams of each soil was treated for 14 days with  $4\frac{1}{2}$  litres of water and filtered; in one case forthwith, and in another lot after the samples had been moistened daily for two months, they then contained respectively 21·40, 8·60, and 32·40 per cent. of moisture. The solutions yielded on analysis the following numbers in parts per 100,000 of air-dry soil:—

Constituents.	1.		2.		3.		Remarks.
	At start.	After 8 weeks.	At start.	After 8 weeks.	At start.	After 8 weeks.	
Humus .....	19·30	22·50	100·60	83·00	158·00	149·30	In Soils 1 and 2, the proportion of lime is small. The quantity of soluble phosphoric acid is large in Soil 2. In Soil 3, the large quantities of magnesium and sulphuric acid are remarkable.
Nitrogen .....	1·89	1·14	3·90	4·22	3·66	4·07	
Ammonia .....	0·19	0·31	0·49	1·22	0·65	0·95	
Nitric acid ....	—	—	—	—	—	—	
Phosphoric acid	0·53	0·40	3·61	4·43	—	0·39	
Potash .....	1·00	1·88	2·93	3·03	3·22	5·14	
Lime .....	1·50	1·42	2·00	1·50	4·80	3·24	
Magnesia .....	—	1·31	—	1·10	—	4·15	
Sulphuric acid .	1·16	2·62	1·66	1·05	4·70	5·98	
Ferrous oxide ..	0·43	—	3·60	4·30	2·20	—	
Silica .....	1·05	4·00	2·30	5·40	2·20	3·64	
Humus soluble in water at 14—18° .	66·0	78·0	678·0	558·0	197·0	187·0	{ In parts 100,000 of pure humus.
Soluble nitrogen .....	0·39	0·39	0·73	0·79	0·33	0·37	{ In parts per 100 of total nitrogen.

The great solubility of beech humus arises from the large amount of undecomposed vegetable refuse it contains, which yields extractive matter to the water. The fertility of these soils seems in some way connected with the solubility of the humus. D. A. L.

**Absorptive Power of Different kinds of Soils for Water.** By P. PICHARD (*Bied. Centr.*, 1883, 728—729).—The soils investigated were clay, silica, and calcium carbonate, in varying degrees of fineness. The author shows that land which has been covered with water will remain saturated for fifty days when it contains 30 per cent. of clay or 10 per cent. of clay and 60 per cent. fine silica. J. K. C.

**Chemical Changes in Soil and Drainage Water.** By F. HOPPE-SEYLER (*Bied. Centr.*, 1883, 725—727).—Samples of black mud from sewers, drains, ditches, wells, ponds, &c., were obtained and employed in this investigation. Note was taken of their mechanical composition, of the action of various reagents upon them, and of their behaviour under different conditions. In their external properties, the samples of mud of different origin were all much alike, separating into a grey upper and a black under layer. The former contains numerous organisms, and the latter consists chiefly of shells of diatomaceæ. At the ordinary temperature, gas bubbles are from time to time evolved from the mud; these contain carbonic anhydride and marsh-gas, and in the absence of ferrous carbonate also sulphuretted hydrogen. A strong fermentation is continually going on, whereby

even the cellulose present is gradually converted into carbonic anhydride, marsh-gas, and hydrogen.

Nitrous and nitric acids are entirely absent in the under layers, and in these, nitrates are speedily converted into ammonium carbonate.

As regards the hygienic condition of a soil, the above results give only negative information. The evolution of carbonic anhydride from a soil cannot be taken as a measure of the quantity of animal matter present, nor can the amount of nitrates and nitrites in the drainage water give any idea of the quantity of impurity, as the existence of all these substances depends on several other variable factors.

J. K. C.

**Contributions to Systematic Manuring.** By P. WAGNER and others (*Bied. Centr.*, 1883, 729—744).—Experiments conducted with the greatest care for five years have, says the author, led to a method as trustworthy as the estimation of phosphoric acid by ammonium molybdate. The first trials were made on a plot of sandy soil divided into 40 lots by means of brick walls sunk 18 inches into the ground. The soil was carefully mixed and made as homogeneous as possible for a depth of 18 inches, and the manure introduced by mixing with the upper layers. Potatoes and barley were the subject of the first series of experiments, but the results obtained were not satisfactory, as several disturbing factors still remained to be eliminated, such as position of the plots, moisture of the soil, &c. In the next series of experiments the dividing walls were made impervious to water by means of cement, and the soil removed to a certain depth from each plot, and replaced by well mixed earth. Barley was also planted round each plot to give similar conditions of light and shade. The results gained were better, but still not satisfactory, and further modifications were introduced, although also without success. The experiments on open land also failed from like causes, and the author holds all results obtained from manuring experiments on this basis to be untrustworthy. Recourse was therefore had to zinc boxes, sunk into an artificial soil, and filled very carefully with the same quantities of sand and earth. The conditions of the soil in the boxes could then be regulated so as to be as nearly as possible alike. The boxes were so arranged that the soil in them was always saturated with water up to a certain height. The same number of seeds were planted in each box, and each experiment repeated at least six times. The results were most satisfactory, the figures obtained agreeing so closely that the mean result could almost be looked upon as free from error.

Careful experiments were made by this method to ascertain the requisite quantity of manure to be used for each kind of seed, and attention was also paid to the accompanying constituents of the manure, and to its coarser or finer condition.

In conclusion the author insists on the above methods as necessary to the carrying out of a tolerably exact manuring experiment, the quantity of moisture in the soil being a factor which must before everything be the same throughout, and the other conditions determining growth must exist in their proper relative proportion.

J. K. C.



**Four-year Rotation Experiments.** By A. VOELCKER (*Bied. Centr.*, 1883, 668—671).—In the present series, the crops grown were wheat, barley, clover, and turnips. Wheat was grown on *plot 1* after clover consumed on the field by sheep, which received in addition 350 kilos. of decorticated cotton-cake per acre; on *plot 2*, after clover consumed on the field, along with 330 kilos. of maize meal per acre; on *plot 3*, after clover consumed on the field without other food, but receiving as manure potash, phosphoric acid, nitrogen, &c., in quantities equal to that in 305 kilos. of cotton-cake per acre; on *plot 4* same as *plot 3*, but receiving, in artificial manures, plant food equivalent in quantity to that of 330 kilos. maize meal per acre. The largest quantity of wheat was obtained on *plot 4*; *plots 1* and *2* were nearly equal; whilst *plot 3* yielded the least.

With barley after turnips consumed on the field without artificial manuring, the best yield was obtained on the cotton-cake plot, the maize meal and unmanured plot being nearly equal, whilst a top dressing of sodium nitrate on the other plot, lowered the yield of corn but raised the quantity of straw. The clover was fed off by sheep, some getting cotton-cake and others getting maize meal in addition. The live weight of the sheep increased to the largest extent with maize meal; the cotton-cake also gave a large increase, whilst the increase from the other plots was small. Swedish turnips yielded best with complete mineral manures and sodium nitrate.

D. A. L.

**Irrigation by Means of Danube Water.** By J. F. WOLFBAUER (*Bied. Centr.*, 1883, 721—723).—10,000 parts of Danube water contain a minimum quantity of 1·294 parts dissolved substances in summer, and a maximum of 2·104 parts in the winter, the maximum and minimum of suspended matter being 3·383 in summer and 0·096 in winter. According to the irrigation project, 18,000 cm. of water per hectare are to be run over a field in the space of 180 days; the soil will therefore receive per hectare 2500 kg. of suspended and 2800 kg. dissolved matter, containing altogether 62 kg. of potash, 46 kg. sodium nitrate, and 4 kg. phosphoric acid. This quantity of potash is, according to the author, sufficient for the production of 2000 kg. of hay, but in order to produce 4000 kg., will require to be supplemented by phosphoric acid in the form of artificial manure, the amount contained in the above quantity of Danube water being insufficient.

J. K. C.

**Manuring Experiments with Potatoes, Beet, and Maize.** By A. NAUTIER (*Bied. Centr.*, 1883, 662—666).—The soil on which the following experiments were made contained 29·4 per cent. of stones above 1 mm. in diameter. The air-dried fine mould contained per cent. :—

OH <sub>2</sub> .	N.	P <sub>2</sub> O <sub>5</sub> .	Humus (containing C).	K <sub>2</sub> O.	CaO.
6·93	0·20	0·25	1·06 (0·64)	0·10	5·97

It is 0·15 m. thick, and therefore contains about 2800 kilos. of phosphoric acid and 2260 kilos. of nitrogen per hectare. The season was bad, there being 411 mm. of rain between May and September.

Some experiments on various kinds of potatoes showed that the best yield, both of tubers and starch, was obtained with Champions, Merveille d'Amérique the next, Early Rose next, then Snowflake, the worst being Saucisse, a French variety. Experiments with potatoes and beet show that on such a soil as the above phosphatic manures are the only ones which cover their cost by increase in crop; moreover, the precipitated phosphate and the superphosphate are of equal manurial value. Nitrogenous manures may be applied in small quantities in fine weather. In experiments on maize for fodder, it was found that stable manure was the only one of any actual value for that plant.

D. A. L.

**Manuring Experiments at Peterhof.** By W. KNIERIEM (*Bied. Centr.*, 1883, 744—749).—Experiments were made with two different soils to ascertain the kind of plant nourishment required. The amount of humus contained in both was large. Varying combinations of potash, phosphates and nitrogen manures were used with each soil, and the crop consisted of oats. In one case, where the soil was very rich in nitrogen, a mixture of potash and phosphates answered best, and without the latter no good yields at all were obtained. The other soil appeared to be in want of all three kinds of manure, as each sort separately gave better results than on the unmanured plots; a nitrogen manure was found to increase the amount of straw, and phosphates gave a larger yield of corn. The quantity of meal in the corn was apparently decreased by the nitrogen manures, whilst the converse took place with the phosphates; and the latter worked equally well whether given in the form of superphosphate or precipitated calcium phosphate.

J. K. C.

**Manuring Experiments.** By v. SCHWERIN (*Bied. Centr.*, 1883, 665—667).—In some experiments made in Löwitz, nitrogenous manures were found efficient on light and medium rye land, and on light warm barley land; whilst phosphatic manures proved valuable on heavy loamy wheat land and on low-lying cold oat land. Flesh meal phosphoric acid was found to be equal in manurial value to superphosphate phosphoric acid on wheat land, and to surpass it on rye land.

D. A. L.

**Silesian Farm without Cattle.** By FISCHER (*Bied. Centr.*, 1883, 671—673).—Since 1871 the author has conducted his farm without cattle, with the exception of a few milking cows, because there is a good demand for fodder and straw in his district. Manures of commerce have, therefore, been employed instead of farmyard manure. The author does not consider this course advisable, unless such special opportunities for the disposal of fodder and straw are offered. Rape seed requires very strong manures, and therefore this crop was grown on those lands which could be manured with the existing farm manure, which consisted chiefly of cuttings from turnips. In his opinion bone meal is the most important manure after farmyard manure. It has been especially favourable to clover in his district. Potassium salts have yielded very variable results; in one manure experiment with potatoes, potassium salts gave even better results than guano. He uses phos-

phoric manures for cereals, or where large quantities are desired, and for green crops nitrogenous, and, when required, potash manures. The author is well pleased with his results, for his farm produce has been steadily increasing since the banishment of cattle.

D. A. L.

**Artificial Manures for Vineyards.** By J. A. NIPPGEN (*Bied. Centr.*, 1883, 708).—The usual manuring for vineyards consists of 400 centners stable manure per morgen every three years. Instead of this the author has employed 300 centners of stable manure and 4 centners of a mixture containing 9–10 per cent.  $P_2O_5$ , 10 per cent.  $K_2O$ , and 2 per cent. N (as ammonium salt), along with 4 centners of kainite, every two years on old vineyards or sickly plants. The results have been very favourable.

D. A. L.

**Cost of Production of Stable Manure.** By A. DETTWEILER (*Bied. Centr.*, 1883, 749–750).—The calculation was made in the case of four herds of cows: After allowing for cost of keep, attention, and depreciation in value, and subtracting the amount realised by the sale of the milk, a result was obtained as to the prime cost of the manure produced, which varied considerably in each case. The cost of the 117 lbs. of nitrogen contained in the year's yield of manure from one cow was estimated variously from nothing to 70 shillings.

J. K. C.

**Wool-dust.** By J. NESSLER (*Bied. Centr.*, 1883, 705).—The author has examined 16 samples of refuse from woollen manufactories, and has determined the amount of fibre, dust, and total nitrogen. The amount of fibre varies from 50 to 7 per cent., the dust from 93 to 50 per cent., the quantity of total nitrogen from 1.08 to 9.68 per cent. From the results obtained, it is shown that the quantity of nitrogen increases with the amount of fibre.

D. A. L.

**Manuring Beetroot with Chili Saltpetre.** (*Bied. Centr.*, 1883, 786).—At a meeting of beet-sugar manufacturers the conclusion was arrived at that Chili saltpetre could be employed with twice its weight of phosphoric acid without harm, but also without much advantage, whilst by itself it was harmful at any time.

J. K. C.

**Manuring with Bone-meal.** By L. KOCH (*Bied. Centr.*, 1883, 709).—The effect of the manure on the harvest was not generally evident. Heavy manuring frequently produced smaller yields than light manuring. "Magnum Bonum" and "Champion" potatoes yielded well. By the use of either large seed, one tuber per hole, or small seed, four tubers per hole, the quantity produced was on an average the same, but the potatoes from the large seed were of better appearance.

D. A. L.

**Gypsum for Manure.** By J. NESSLER (*Bied. Centr.*, 1883, 705).—The author has examined gypsum from various localities with regard to the fineness and percentage of calcium sulphate. Twelve specimens were examined, that from Trüb, in Hornstein, being the

finest; whilst the richest in calcium sulphate was from Kray, in  
Achern. D. A. L.

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## Analytical Chemistry.

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### Employment of Boric Acid and Hæmatin in Alkalimetry.

By A. GUYARD (*Bull. Soc. Chim.* [2], **40**, 422—423).—The author recommends boric acid for the preparation of a standard acid solution in alkalimetry. A solution of commercial hæmatin, the colouring matter of Campeachy wood, is used at the indicator. W. C. W.

**Value of Lenz's Method for the Purification of Hydrogen Sulphide.** By R. OTTO (*Ber.*, **16**, 2947—2954).—The author having doubts as to the possibility of hydrogen arsenide being sufficiently basic in its properties to combine with hydrochloric acid, repeated the process by which Lenz (this vol., p. 215) asserted he had freed hydrogen sulphide from traces of arsenic. Hydrogen sulphide, evolved from commercial sulphide of iron and commercial hydrochloric acid, both known to contain arsenic, was passed through the water and hydrochloric acid solutions at 60—70°, as required in Lenz's process, then through concentrated caustic soda, and finally through pure nitric acid. On testing these in a large number of trials arsenic was always found in the nitric acid, but not in the hydrochloric acid solutions; and the author supposes that the hydrochloric acid, employed for washing the gases by Lenz, may have contained some foreign substance capable of absorbing hydrogen arsenide, possibly chlorine. A. B.

### Preparation of Concentrated Nitromolybdic Acid Solution.

By A. GUYARD (*Bull. Soc. Chim.* [2], **40**, 423—425).—A saturated solution of ammonium molybdate is poured into 20 c.c. of dilute nitric acid (prepared by mixing equal volumes of strong acid and water) until a permanent precipitate begins to form. The acid must be kept perfectly cold during the process. The author considers it advisable not to use more than 20 c.c. of dilute acid for each operation. W. C. W.

**Determination of Ammonia as Nitrogen in Manures.** By W. MASSALSKI (*Bull. Soc. Chim.*, **40**, 18—21).—The researches of Knop, Mehu, and others have established that ammonium salts when heated with sodium hypobromite, in presence of excess of soda and of glucose, evolve all their nitrogen as such. The presence of the glucose does not, as usually supposed, reduce any nitrates which may be produced, but it prevents their formation. In this paper an apparatus is described for the determination of nitrogen in manures containing ammoniacal compounds, and the results were found to agree with those obtained by the soda-lime process. However, the application of the method proposed is rather restricted, for powdered horn,

meal, or fish guano only give up from one-quarter to one-tenth of their nitrogen to sodium hypobromite. Ordinary guano gives up about four-fifths of its nitrogen, and it is suggested that it is desirable to ascertain by experiment whether the whole of the nitrogen of guano can be considered to be ammoniacal, or part ammoniacal and part so-called organic nitrogen.

V. H. V.

**Estimation of the Total Nitrogen in Manure.** By E. DREYFUS (*Bull. Soc. Chim.* [2], **40**, 267—271).—When manure contains nitrogen in the different forms of nitrates, ammonia, soluble and insoluble organic matter, the total nitrogen is best estimated by the following process, which yields very exact results. 1 gram of the manure is heated with sulphuric acid in a small glass vessel until the nitric acid is expelled, and fumes of sulphuric acid begin to come off. When the solution is cold, sufficient calcium carbonate is added to form a perfectly dry mixture. The nitrogen in the mixture is determined in the usual way by means of soda-lime; this gives the total organic nitrogen plus the ammonia. The nitrogen present as nitrate is determined in another portion of the sample by Schloesing's method. Corrections for temperature and pressure may be avoided by comparing the volume of gas obtained with that evolved from a normal solution of sodium nitrate (66 grams per litre).

To prepare soda-lime, 3 parts of quicklime are slaked with 3 parts of water containing  $1\frac{1}{2}$  of caustic soda, and  $\frac{1}{3}$  of a part of pure sugar. On heating the soda-lime, the sugar is decomposed, and any traces of nitrate contained in the soda are destroyed.

W. C. W.

**A Cause of the Differences noticed in the Estimation of Superphosphates.** By M. MÄCKER (*Bied. Centr.*, 1883, 751—752).—The author finds that the amount of soluble phosphoric acid in superphosphates decreases somewhat rapidly when the latter is packed in tin canisters, owing to the formation of insoluble phosphates of iron and tin. This may reasonably be supposed to be the cause of the differences in the analyses of superphosphates, some samples having probably been packed in these vessels, and thereby undergone change, while the original stock has remained unaltered.

J. K. C.

**Gladding's Process for the Estimation of Retrograde Phosphates.** By MILLOT (*Bull. Soc. Chim.*, **40**, 101—104).—In order to obtain an accurate estimation of the retrograde phosphate, it is necessary to use a reagent which will dissolve it without attacking that portion of the original phosphate which has escaped the action of the sulphuric acid. For this purpose Gladding has proposed a slightly ammoniacal solution of ammonium citrate of density 1.07; the superphosphate is heated for about an hour at the temperature of 70°. In France a similar process is in vogue; the superphosphate is placed in contact for 12 to 15 hours with a very concentrated and ammoniacal solution of ammonium citrate. In this paper analyses by these two processes are cited, and the results obtained are found to be comparable in the case of aluminium and ferric phosphates.

V. H. V.

**Separation of Alumina, Ferric Oxide, and Titanic Oxide.** By E. COHEN (*Jahrb. f. Min.*, 1884, 1, Mem., 186—187).—The author recommends the following as the most exact method of separating alumina, ferric oxide, and titanic oxide. The precipitate of the three hydroxides produced by ammonia is dissolved in hydrochloric acid. The alumina is separated by sodium hydroxide, and the acid solution of ferric oxide and titanic oxide is reduced with sulphurous acid in the cold (on heating, a portion of the titanic oxide is precipitated). Tartaric acid is added until ammonia gives no precipitate. The FeO is precipitated by ammonium sulphide. The TiO<sub>2</sub> obtained from the filtrate by evaporating and fusing, must be taken up by acid potassium sulphate and precipitated from the dilute solution by boiling in order to obtain it pure. B. H. B.

**Detection of Manganese in Commercial Zinc-dross and in Calamine. Detection of Bismuth in Lead.** By A. GUYARD (*Bull. Soc. Chim.* [2], 40, 420—421).—The zinc-dross or calamine is dissolved in sulphuric acid and the solution subjected to electrolysis, platinum electrodes being employed. If manganese is present, the positive pole is surrounded by a purple coloration due to permanganic acid.

To detect bismuth in metallic lead, make a piece of the lead into the positive electrode in the electrolysis of a solution of pure zinc sulphate. Dissolve the deposit on the negative electrode in dilute sulphuric acid, and if a dark residue remains, test it for bismuth.

W. C. W.

**Use of Air Saturated with Bromine in the Precipitation of Manganese.** By A. WOLFF (*Zeitschr. Anal. Chem.*, 22, 520—522).—A current of air is made to pass through a wash-bottle containing water and bromine, it thus becomes saturated with the vapour of bromine, and is then passed into the strongly ammoniacal solution of manganese acetate. The current is continued until the brown flakes of the hydrated manganese peroxide have separated, the precipitation being usually complete in 20 minutes. The bromine wash-bottle is then replaced by one containing ammonia, through which the current of air is continued for another 15 minutes. The solution is then ready for filtration, and if ammonium instead of sodium acetate has been employed for separating the iron, the precipitate may be at once ignited and weighed as Mn<sub>3</sub>O<sub>4</sub>. P. F. F.

**Estimation of Chromic Oxide by Titration.** By B. PAWOLLECK (*Ber.*, 16, 3008—3009).—This method depends on the fact that chromic oxide is readily oxidised by nitric acid and potassium chlorate, whilst cold dilute nitric acid has no oxidising action on a ferrous salt, and is of use in the estimation of commercial chromic salts and chromic hydroxides. The process is as follows. The weighed substance containing from 0.3 to 0.5 gram Cr<sub>2</sub>O<sub>3</sub> is dissolved in a flask containing 25 c.c. nitric acid, sp. gr. 1.4, and slowly with gentle boiling crystals of potassium chlorate (about 2 grams for the above-mentioned quantity of oxide) are added until the liquid has the pure

reddish-yellow colour of a chromic acid solution: with practice this is easily recognised. The solution is boiled until the decomposition products of the chlorate are driven off, cooled, diluted to about 350 c.c. with water, and titrated in the ordinary way with ferrous ammonium sulphate solution. If the substance for analysis is already in solution, concentration is necessary before oxidation. The method may also be used for ignited or insoluble chromic oxide, but complete oxidation is more difficult. The process has been carefully investigated and verified by comparison with the ordinary method of oxidation by fusion with alkaline carbonates, and has been found much quicker and equally accurate. A. B.

**Determination of Small Proportions of Alcohol in Viscous Liquids.** By E. BORGMANN (*Zeitschr. Anal. Chem.*, **22**, 534—535).—100—200 grams of the liquid are distilled in a current of steam until about 100 c.c. of distillate has collected. The distillate is then redistilled in the ordinary way, the first two-thirds which pass over being collected and used for the determination of sp. gr. P. F. F.

**Halymetric Determination of Alcohol in Beer.** By KLEINERT (*Zeitschr. Anal. Chem.*, **22**, 505—512).—The author finds that shaking beer for the prescribed 15 minutes does not render its weight constant by the elimination of the dissolved carbonic anhydride, but that on continuing the agitation a further loss takes place. Moreover, different varieties of beer require different periods of agitation. The determination of the carbonic anhydride is thus liable to serious error, as are also those of the alcohol and extract, which depend on this determination. The same uncertainty also exists as to the length of time for which the beer should be shaken up with the salt in order that saturation may take place. P. F. F.

**Ratio of Glycerol to Alcohol in Beer.** By E. BORGMANN (*Zeitschr. Anal. Chem.*, **22**, 532—534).—The author has previously investigated the ratio of glycerol to alcohol in wine (*Abstr.*, 1883, 518). The ratios found for different kinds of beer were—

	Alcohol.	Glycerine.
Maximum.....	100	5.497
Minimum .....	100	4.140
Mean.....	100	4.803

The ratio thus varies within very narrow limits, and this result is of particular importance, as an artificial admixture, either of spirit or glycerol, can be inferred if the above ratio is appreciably disturbed. The samples of English beer examined, although of much greater alcoholic strength than the others, exhibited the same ratio.

P. F. F.

**Determination of Acetic Acid in Wine by Distillation with Steam.** By B. LANDMANN (*Zeitschr. Anal. Chem.*, **22**, 516—519).—50 c.c. of wine, to which a few grains of tannin have been added, are



placed in a small flask. A rapid current of steam is conducted through the wine, which is also heated to boiling, and the escaping vapours are passed through a condenser and collected in a graduated flask. The distillation is carried on until 200 c.c. of liquid are collected in the receiver. The distillate is titrated as acetic acid.

P. F. F.

**Reaction of Ashes from Wine.** By CHIAPPE (*Bied. Centr.*, 1883, 790).—The alkaline reaction of wine ashes cannot be taken as an indication of the absence of free sulphuric acid in the wine. The ash will be alkaline if the sulphuric acid is not sufficient to combine with the whole of the bases, and even sulphates when incinerated will often be reduced to alkaline sulphides, which give an alkaline reaction.

J. K. C.

**Determination of Sugar in Beetroot.** By K. STAMMER and E. SOSTMANN (*Bied. Centr.*, 1883, 779—782).—According to Stammer the different methods of extracting sugar from beet do not yield concordant results on polarisation. To obviate this difficulty, he digests the crushed root with 92 per cent. alcohol for an hour, makes up to a certain quantity, and finds that the liquid so obtained gives exact results. As the method, however, is tedious, he prefers to grind the root up in a mill until it becomes an impalpable pulp, and then shake up with cold 92 per cent. alcohol, which extracts the whole of the sugar.

Sostmann digests beet pulp with 80 per cent. alcohol, treats with lead acetate, filters, and determines the sugar by polarisation in the filtrate, making the correction suggested by Degener.

J. K. C.

**Examination of Spices.** By E. BORGMANN (*Zeitschr. Anal. Chem.*, 22, 535—537).—The author has determined the alcoholic extract and ash in a number of samples of various condiments—white and black pepper, cinnamon, cloves, mace, and allspice.

P. F. F.

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### Technical Chemistry.

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**Sanitation of Large Towns and Value of the Refuse Matter from them.** By A. MÜLLER (*Chem. Centr.*, 1883, 706—708).—The author enumerates the various points to be observed in order to effect the sanitation of towns, and some of the methods at present employed for the disposal of sewage and otherwise rendering it harmless. The “water carriage systems,” the separating system, the earth system, &c., are referred to. In order to utilise sewage for agricultural purposes, it must be treated on a manufacturing scale, concentrated so as to be stored, easily conveyed from place to place, and rendered useful as manure. Two methods of concentration are alluded to: Liernur and Podewil’s process of evaporation in a vacuum, and Buhl

and Keller's process of precipitation, pressing, and distillation. The cost is lower the more concentrated and pure the refuse matter, and the more readily the material is conveyed to the works. Swedish air closets fill the first of these conditions, and Liernur's pneumatic process the second, wherein the material is conducted through pneumatic pipes by means of steam power.

No use other than manurial has been found as yet for sewage. The incineration system, where all the organic matter is burnt, although good in some cases, can never be taken into consideration for general application.

D. A. L.

**Notes on the Soda Industry.** By SCHEURER-KESTNER (*Bull. Soc. Chim.*, 40, 75—83).—The memoir contains the results of the investigations of Chance, Brock, and Hurter on the sulphur regeneration process of Schæffner and Helbig, together with some critical remarks offered by the author.

Part I. In *Chance's investigations*, conducted on a large scale, the resultant hydrogen sulphide was not decomposed by sulphurous acid in a concentrated calcium chloride solution to form sulphur; but it was collected in gasometers, and finally burnt to produce sulphuric acid. The soda waste is introduced by a shaft into a cylindrical reservoir, furnished with an agitator, and the temperature is then raised to 50°; the gas evolved passes through a layer of water, and then a series of vertical pipes, into a gasometer. To prevent loss and smell, the water of the gasometer is covered with a layer of an oil known to the trade by the name of *blue* or *dead* oil. In the second or carbonating process, the admixture of calcium chloride and magnesia is transferred to a vertical cylinder analogous to that used in Weldon's manganese recovery process, warmed either externally or internally by steam and carbonic anhydride passed in. The former method is more economical, but the latter more practical. The calcium carbonate formed can be separated from the magnesium chloride by filtration through filter-presses.

As regards the pecuniary gain, Chance has calculated a profit of £66 for a quantity of waste corresponding with 300 tons sodium sulphate. But it is pointed out that as the price of pyrites will soon be lowered, this profit will be considerably diminished. As regards the decomposition of hydrogen sulphide by sulphurous acid, Chance was unable to prevent the formation of sulphuric and the polythionic acids. Analyses of the regenerated calcium carbonate are appended below:—

Calcium carbonate.....	71—79	per cent.
Calcium sulphate .....	3·9—4·6	„
Calcium chloride .....	0·25—1·51	„
Magnesium carbonate .....	0—1·77	„
Magnesia.....	1·67—3·2	„
Carbon.....	3·0—5·8	„
Silica.....	0·3—3·30	„
Ferric oxide .....	1·0—2·3	„
Alumina .....	0·76—0·96	„
Soda.....	0·70—1·75	„

In conclusion, the author remarks that the only hope of the competition of the Leblanc with the ammonia-soda process rests not on the regeneration of sulphur, but rather on the production and rise in price of the hydrochloric acid.

Part II. *Employment of Chalk Mud*.—Brock has employed the chalk mud from the Schæffner-Helbig process for the production of crude soda. The following mixture was introduced into the revolving furnace:—

Sodium sulphate.....	100	parts
Chalk mud .....	200	„
Coal .....	40·3	„

The crude soda obtained possessed the following composition:—

	Per cent.	
Sodium oxide.....	21·3	
Sodium sulphate .....	1·2	} or 25Na <sub>2</sub> O
Sodium chloride .....	2·88	
Sodium sulphide .....	0·55	

The amount of chloride is very large, and probably arises from an imperfect washing of the chalk mud. The operation lasted  $2\frac{3}{4}$  hours; whilst only 2 hours are required with dry chalk.

Part III. Hurter has investigated the same subject, employing various mixtures of chalk mud, sodium sulphate, and coal, and obtained crude soda containing 24 per cent. sodium oxide, and 3·88—4·08 sodium chloride (or 25 Na<sub>2</sub>O). Mactear considers that a more perfect washing of the chalk mud could be effected by warm water, and remarks that the soda manufacturers cannot rely on large profits from the sale of sulphur. The sole gain of the Schæffner and Helbig process will rest on the production of sulphuric acid. V. H. V.

**Manufacture of Sevres Blue.** By C. LAUTH (*Bull. Soc. Chim.*, 39, 435—443).—In this paper a full description is given of the manufacture of the so-called refractory blue of Sevres, and of the various accidents attending its firing.

The colour consists of a fritted mixture of 15 parts cobaltic oxide and 85 parts of pegmatite; it forms a blackish-grey mass. It is applied on the enamelled and kilned porcelain by working it up with turpentine, oxidised by the air, and thus rendered viscous. After application, the porcelain is dried at a gentle heat to expel the turpentine, and finally it is muffled at a red heat to completely destroy any turpentine present.

The process is frequently unsuccessful, however, and the failure is due to three causes, known by the names of (i) crazing (*grésillements*); (ii) displacements (*déplacement*), and metallisation. In the first case, the enamel, instead of being smooth, is rough and crinkled, being covered with blebs; in the second the colour is not uniformly distributed, but accumulated in places; and on the third the surface of the enamel presents black mirror-like spots. Of these accidents the first is practically irremediable, and on investigation was found to arise from the introduction within the kiln of organic

substances, especially hydrocarbons, which exert a reducing action on the colour. In practice, it is due to an imperfect circulation of the products of combustion within the kiln, whereby the porcelain is exposed to this action. The second accident, which is far less frequent, is caused by an imperfect volatilisation and decomposition of the turpentine; vapours of heavy hydrocarbons are evolved, which condense on the red-hot porcelain within the kiln. Finally, the third accident or metallisation is due to an insufficient burning of the porcelain; it can be rectified by raising the temperature.

V. H. V.

**Purification of Alcohols.** By L. NAUDIN (*Bull. Soc. Chim.* [2], 39, 626—646).—This paper contains an account of an industrial method of the purification of alcohol and alcoholic and saccharine liquors, by means of the copper-zinc couple, and subsequently by electrolysis. The crude alcohol is pumped into a vertical cylinder, across which are serpentine-shaped bars of zinc, on which copper has been deposited; the alcohol remains in this vessel for two days. It is then either distilled or submitted to a powerful electric current from a Siemens dynamoelectric machine.

In conclusion, a table is given to show the pecuniary profit of this process of purification as against the former method of frequent rectifications.

V. H. V.

**Analyses of Wine.** By J. MORITZ (*Zeitschr. Anal. Chem.*, 22, 513—515).—The author has analysed a number of German wines

Description.	Acidity ( $C_4H_6O_6$ ). Per cent.	Extract. Per cent.		Mineral matters. Per cent.	Alcohol. Per cent. by volume.	Phosphoric acid. Per cent.	Glycerol.	Specific gravity.	Polarisation.
		Direct.	Calculated from Hager's table.						
Neuberg, <sup>1</sup> 1878	0.52	2.3	2.3	0.21	9.8	0.018	0.899	0.9980 (18.5°)	± 0
Lindlesberg, 1878	0.67	2.05	2.33	0.21	9.4	0.020	—	0.9974 (17°)	± 0
Traminer, 1878	0.63	1.81	2.23	0.198	9.1	0.0313	0.83	0.9966 (15.6°)	± 0
Stein, 1875..	0.64	1.99	—	0.236	9.0	0.0375	0.58	0.9978 (15°)	± 0
Hohenburg, 1878	0.51	2.05	2.14	0.190	9.8	0.0370	0.75	0.9955 (15°)	± 0
Lorcher, (Red), 1876	0.47	—	—	—	9.9	SO <sub>3</sub> 0.0165	—	—	± 0

from undoubted sources, the results are, therefore, of interest as extending our knowledge of the composition of pure wine. A few only of these results can be recorded here. P. F. F.

**Analyses of Wines from Anjou.** By A. BOUCHARD (*Bied. Centr.*, 1883, 782—783).—Eighteen white wines from Layon contained:—

	Alcohol. Per cent.	Extract. Per cent.	Specific gravity.
Maximum.....	17·5	4·66	1·020
Minimum.....	10·9	2·39	0·988
Mean.....	14·8	3·66	1·002

Eighteen white wines from the Loire district:—

Maximum.....	17·1	3·89	1·020
Minimum.....	10·0	1·75	0·976
Mean.....	14·09	2·99	0·995

Eighteen red wines:—

Maximum.....	13·2	2·90	0·999
Minimum.....	8·0	1·69	0·990
Mean.....	10·88	2·23	0·995

J. K. C.

**Analyses of Wines from Palestine, &c.** By A. STUTZER (*Bied. Centr.*, 1883, 790).—The following are the maxima and minima percentages of some of the constituents:—Alcohol, 15·34 and 9·27; glycerol, 2·0 and 0·29; sugar, 9·82 and 0·10; and ash, 1·164 and 0·126 per cent. J. K. C.

**Influence of "Plastering" on the Composition of Wine.** By L. MAGNIER DE LA SOURCE (*Compt. rend.*, 98, 110—113).—Plastering modifies the chemical characters of the colouring-matter of the wine, and not only does the calcium sulphate decompose the potassium hydrogen tartrate with formation of calcium tartrate, potassium sulphate, and free tartaric acid, but it also decomposes the neutral organic compounds of potassium which exist in the juice of the grape. The proportion of calcium in the wine is not sensibly increased.

C. H. B.

**Souring of Wine.** By P. CARLES (*Bied. Centr.*, 1883, 790).—The author remarks on the changes undergone by wine in this process. A diminution takes place in the amount of extract and gum; sugar and other substances which reduce Fehling's solution, but are not thrown down by lead acetate, disappear completely. The glycerol decreases in quantity, as does also the cream of tartar, while the free tartaric acid disappears altogether, and the barium slowly decomposes into ulmic bodies. On the other hand, the potash increases in quantity, owing to the decomposition of the deposit of cream of

tartar. When the sickness has not gone too far, it may be remedied by the addition of new wine rich in tartaric and tannic acids.

J. K. C.

**Influence of Temperature on the Fermentation of Must.** By H. MÜLLER (*Bied. Centr.*, 1883, 783—785).—The higher the temperature, the sooner the fermentation is finished; at low temperatures, a moderate fermentation takes place, which becomes more violent as the liquid becomes warmer, and reaches a maximum at 27°. By the employment of high temperatures, a must rich in sugar can be converted into a wine only feebly alcoholic, sweet, and yet having lasting properties. Medium musts are best fermented at from 20° to 24°, and this temperature is reached when the fermentation begins at 15°.

J. K. C.

**Removal of Juice from Sugar-beet.** By A. KLEWITZ and G. KRIEGER (*Bied. Centr.*, 1883, 731).—The authors have constructed a diffusion apparatus for removing the juice from sugar-beet with a smaller quantity of water. The apparatus consists of several compartments, separated by metal sieves, the water employed is poured in the first of a series charged with beet, and then passes through all subsequent compartments, gradually becoming richer in extract. The exhausted material is also passed through the series; the first only being replenished with fresh matter for extraction.

D. A. L.

**Valuation of Gelatin.** By F. PROLLIUS (*Dingl. polyt. J.*, 249, 425).—The author has determined the amount of ash, water, and insoluble matter (residue insoluble in hot water) in various kinds of gelatin. To ascertain the gelatinising property 1 part of the sample was dissolved in 90 parts of water, filtered, and the degree of viscosity determined.

	Ash.	Water.	Insoluble.	Time required for the solution to run out.
	p.c.	p.c.	p.c.	seconds.
Astracan from Schmidt and Dihlmann, Stuttgart.....	0·20	16·0	2·8	507
Ditto, from a collection .....	0·37	18·0	0·7	485
Ditto, fine iridescent Russian quality, Tübingen collection .....	1·20	17·0	1·0	500
Ditto, Russian, from Gehe of Dresden.....	0·80	19·0	3·0	491
Ditto, in laminæ, from Gehe.....	0·50	19·0	0·4	480
Ditto, in threads, known as Hamburg threads .....	0·40	17·0	1·3	477
Hamburg isinglass.....	1·30	19·0	2·3	470
Another quality.....	0·13	19·0	5·2	—
Rolled northern fish bladder.....	3·20	1·5	10·8	467
Icelandish bladder.....	0·60	17·0	21·6	463
Indian isinglass .....	0·78	18·0	8·6	437
Yellow, quality unknown.....	2·30	17·0	15·6	360

To judge of the purity of isinglass, it is also recommended to subject the sample to microscopic examination. D. B.

**Composition of Roasted Chicory.** By A. PETERMANN (*Bied. Centr.*, 1883, 843—845).—The following are analyses of pure chicory, one sample being coarse, the other fine :—

	Coarse grains.	Fine powder.
Water (100—105°).....	16·28	16·96
Glucose.....	26·12	23·76
Dextrin, inulin.....	9·63	9·31
Albuminoids.....	3·23	3·66
Colouring matter and bitter extractive....	16·40	17·59
Ash.....	2·58	2·55
Albuminoids.....	3·15	2·98
Fat.....	5·71	3·92
Cellulose.....	12·32	13·37
Ash.....	4·58	5·87

57·96 per cent.  
soluble in hot  
water.

26·14 per cent.  
insoluble.

The ash was somewhat higher than usual, but was quite white; as the ash of pure samples varies much, owing to the imperfections of manufacture, it is quite inadmissible to judge of the purity of a sample of chicory by its ash. E. W. P.

**Soap Varnishes.** By E. ANDRES (*Pharm. J. Trans.* [3], 14, 169).—These varnishes are valuable on account of their cheapness, their resistance to water, and their elasticity. Such a varnish can be made by dissolving tallow-soap in boiling water, filtering hot through cloth, and precipitating with a boiling solution of alum; the precipitated stearate of alumina is washed and dried, heated on a water-bath until transparent, and then stirred into turpentine; this mixture is heated nearly to boiling until it forms a thick varnish, which can be thinned with turpentine. A waterproof varnish for cloth or paper is made by dissolving iron or aluminium stearate in carbon bisulphide or benzene. Varnish for gilding is prepared from resin soap, which is made by stirring and boiling for two or three hours 100 parts of powdered resin with 50 parts of soda, dissolved in 100 of water until the mixture is clear. The soap is mixed with 100 parts of water and 15 parts of steeped glue, and heated until the whole is dissolved. This is a quick drying varnish, but can be made slow drying by adding 10 to 20 parts of glycerol 28° B. The resin soap, mixed with 5 per cent. ammonia, forms a cheap and durable vehicle for paints.

D. A. L.



## General and Physical Chemistry.

---

**Spectra of Silicon Fluoride and Hydride.** By K. WESENDONCK (*Wied. Ann.*, **21**, 427—437).—As the author observed in a bought Geissler tube containing silicon fluoride the spectrum of carbonic oxide, he examined the result with especial reference to the spectra of silicon compounds, and the cause of the presence of that of carbonic oxide. Silicon fluoride was prepared in the usual way in an apparatus made entirely of glass, and fitted with stopcocks; this was connected with a Geissler's tube. The apparatus was first exhausted, then the acid allowed to come in contact with a mixture of pure glass and fluorspar, and the apparatus again frequently exhausted until the gas present was in all probability pure. However, with all this care the spectrum of carbonic oxide was always visible, and mixed with that of silicon fluoride. At comparatively high pressures, when the discharge gave a continuous cylinder of light, there was observed a more or less continuous carbonic oxide spectrum with the characteristic eight blue bands of silicon tetrafluoride; with decrease of pressure, the spectrum varied precisely in the same manner as that of carbonic oxide, the eight blue bands became clearer, and bands in the violet appeared. With the introduction of a Leyden jar in the circuit, Swan's carbon spectrum became visible. In another form of apparatus in which the stopcocks and all lubricating material was avoided, the same phenomenon was observed. As the cause was proved not to be due to the action of the gas on the electrode, its probable explanation lies in the great avidity of silicon tetrafluoride for water. If by the contact of the gas with water a little oxygen were set free, the latter would possibly oxidise immediately any trace of carbon containing substances, such as dust, which might be present.

The spectrum of a mixture of silicon hydride and hydrogen (formed by Wöhler's process) gave in narrow tubes only the spectra of carbonic oxide and hydrogen; in broad tubes under high pressure a number of lines which were observed in the silicon fluoride spectrum were visible, although the characteristic blue bands were absent; possibly the latter are peculiar to silicon fluoride. V. H. V.

**Fluorescence of Calcspar.** By E. LOMMEL (*Wied. Ann.*, **21**, 422—427).—A red-brown fluorescence of calcspar can best be observed when parallel light rays, rendered convergent by a lens, are made to pass through a cube of calcspar; it is rendered more marked if the light has previously filtered through blue cobalt glass or green glass. The phenomenon is unaltered whether the bundle of rays passes through the crystal normally or parallel to the axis, or when it is not polarised, or polarised in any direction. The emitted spectrum extends from 35 to 65 (Bunsen's scale), and is most marked about 44. The light emitted by calcspar in the phosphoroscope has the same

colour tone and the same spectrum, and differs from that observed in direct radiation only in intensity. It is evident that in both cases the same phenomenon is dealt with, and thus the question is opened whether Becquerel's nomenclature of phosphorescence of long and of short duration, respectively fluorescence or phosphorescence so-called, does not best represent the relation between these two modifications.

The word phosphorescence is generally used for radiation of light visible only in a darkened position, but the conception implied in this expression is far too wide for the phenomenon. The word fluorescence generally means the self-illumination of a body during the radiation of light upon it, although there is nothing in the word which implies a permanence of illumination after the radiation has ceased. It is here proposed to retain the word *fluorescence*, and to substitute for phosphorescence the phrase *phosphorescence of illumination*. As in the latter case the self-illumination continues for an hour or more after the source of light is removed, but in the former only a fraction of a second, the phenomena are sufficiently distinct for distinction of nomenclature.

In order to determine the kind of rays most efficacious for causing the fluorescence of calcspar, a cube of it was placed in various parts of the spectrum, it was observed that the green rays between E and b were most effectual. It follows, then, that the maximum of absorption of calcspar lies between the same limits. This result is possibly connected with the phenomenon of double refraction and dispersion of calcspar. In a former memoir the author has shown that this latter is conditioned by two peculiar vibrations of its molecules; the wave-length of the one normal to the axis =  $\lambda_0 = 0.1301\mu$ , that of the other parallel to the axis  $\lambda'_0 = 0.0874\mu$ . But integral multiples of these numbers,  $4\lambda_0 = 0.5204\mu$  and  $6\lambda_0 = 0.5244\mu$ , approximately correspond to the wave-lengths for E ( $\lambda = 0.5269\mu$ ) and b ( $\lambda = 0.5183\mu$ ). Hence it follows from this theory that substances can absorb not only rays whose wave-lengths are equal to those of their own vibrations, but also rays whose wave-lengths are multiples or sub-multiples of them (indirect absorption).

V. H. V.

**Electromotive Force in Terms of Chemical Energy.** By S. CZAPSKI (*Wied. Ann.*, 21, 209—243).—Thomson and Helmholtz have expanded the Joule-Lenz law regarding the development of heat during electrolysis thus: the electromotive force of a galvanic cell (without polarisation) can be expressed in terms of the electrothermic energy of chemical processes caused by the passage of the current. The researches of Bosscha, Braun, Wright, and others have tended rather to disprove the validity of this law. Recently Helmholtz has inferred from experiments that the value of the thermic energy of the chemical processes, not transformed into electric energy, is related to the change of electromotive force induced by change of temperature. The experiments described in the present memoir point to the conclusion that those galvanic cells which do not convert all their chemical energy into electric work, show decreasing electromotive force with rise of temperature, and conversely those which work at the cost of their own heat capacity, show increase of electromotive force with rise of tempe-

perature. In the experiments, the following conditions were observed as far as possible: 1st, the E.M.F. of the cell to be examined was compared with that of a constant normal cell whose E.M.F. had been determined in absolute units; 2nd, the examined cell was sufficiently constant, free from polarisation changes, and so composed that its electrolytic processes were reversible and defined; its temperature was kept constant. The standard cell was of the composition  $\text{Zn} | \text{ZnCl}_2 | \text{Hg}_2\text{Cl}_2 | \text{Hg}$ ; its E.M.F., as also that of the examined cell, was estimated by the Bois-Reymond compensation method.

The following combinations were examined:

$\text{Zn} | \text{ZnCl}_2 \text{ solution} | \text{AgCl} | \text{Ag}$ ;  $\text{Zn} | \text{FeCl}_2 \text{ solution} | \text{AgCl} | \text{Ag}$ ;  
 $\text{Zn} | \text{ZnBr}_2 | \text{Hg}_2\text{Br}_2 | \text{Hg}$ , and  $\text{Cd} | \text{CdCl}_2 | \text{Hg}_2\text{Cl}_2 | \text{Hg}$ .

The results collected from the paper illustrate the proposition enunciated above, although they must be considered only as preliminary and approximate; for the heats developed or absorbed in the various chemical changes have not been fully investigated.

Of the table below in the first column is placed the temperature, in the second the E.M.F. in volts compared with the standard element, in the third the work done by the current in calories, in the fourth the chemical heat in calories, in the fifth the difference between the two last values, and in the sixth the value calculated from the formula  $Q = \theta \frac{dp}{d\theta J} E$ , in which  $Q$  = quantity of heat,  $p$  difference of potential,  $E$  electric quantity,  $J$  Joule's equivalent.

Cell.	$\text{Zn}   \text{ZnCl}_2 \text{ sol.}   \text{AgCl}   \text{Ag}.$				
Temp.	E.M.F.	Work equivalent.	Chemical heat.	Diff.	$\theta \frac{dp}{d\theta J} E.$
16·00	0·9149	44·32	54·08	- 9·76	- 3·39
14·00	0·9155				
00·00	0·9183				
Cell.	$\text{Zn}   \text{FeCl}_2   \text{AgCl}   \text{Ag}.$				
31·15	0·576	33·00	17·40	+ 15·60	+ 4·85
20·00	0·886				
00·00	0·5282				
Cell.	$\text{Cd}   \text{CdCl}_2   \text{Hg}_2\text{Cl}_2   \text{Hg}.$				
37·00	0·7130	34·76	13·70	+ 20·86	+ 2·65
28·00	0·7118				
20·00	0·7106				

The author proposes to continue his researches in the same direction.  
V. H. V.

**Electric Properties of Flames.** By J. KOLLERT (*Wied. Ann.*, 21, 244—273).—This investigation is a continuation of Hankel's re-

searches on the electric properties of the Bunsen and alcohol flames. The method of experiment was as follows:—

A spiral of platinum was placed in the flame symmetrically with its axis, and connected with one pole of a Hankel's electrometer, the other pole being in connection with the burner; the electrometer was also connected by a commutator with the poles of a zinc-copper pile conducting to earth.

The principal results of the investigation are as follows:—

(I.) The difference of potential is dependent on the material and the temperature of the mouth of the burner; an electropotential series of the materials of which the burners are constructed can be arranged, of which iron is the most negative.

(II.) The difference of potential is also conditioned by the position of the spiral; the point at which the greatest electromotive force is produced coincides probably with that of maximum temperature. This latter result probably represents the sum of several conflicting causes: firstly, by the rise of temperature the platinum is positively electrified; secondly, by contact with the hydrogen and carbonic oxide gas it is negatively electrified; and thirdly, in the cooler parts of the flame it is positively electrified by contact with steam and carbonic anhydride. As regards the second of these points, the experiments of Deville tend to show that the higher the temperature, the greater proportion of free hydrogen and carbonic oxide present; whilst Grove has shown that platinum is negatively electrified when in contact with these gases.

(III.) The results obtained by the author agree with those of Elster and Geitl; the former finds for the E.M.F. of a platinum spiral in a Bunsen flame = 1.95 Daniell, in an alcohol flame = 1.43 Daniell; while the latter obtained the values 1.92 and 1.44 Daniell respectively.

V. H. V.

**A New Method of Generating Electricity.** By J. A. KENDALL (*Chem. News*, 49, 49—51).—The author has observed that hydrogen passing through a red-hot platinum plate can serve as an element of a galvanic combination. Various methods of applying this discovery have been adopted, and one of the best apparatus consists of two platinum tubes of different sizes closed at one end, made from metal  $\frac{1}{100}$  inch thick; the smaller tube can be connected with a hydrogen supply, and arranged at any desired height in the centre of the large tube, the intervening space between the two tubes being filled with a suitable medium. When this arrangement is heated in the oxidising flame, the internal and external metallic portions being connected with a galvanometer by means of conducting wires, no deflection is produced until hydrogen is supplied to the inner tube. The production of electricity increases with the temperature, and is proportional to the extent of surface heated; most powerful effects are observed when the metallic coating is in a finely divided form; whilst the best results have been obtained when the inner metal is much thicker than the outer coating, in fact, the cell is quite spoilt when the reverse is the case, owing to the accumulation of hydrogen on the inner plate. The E.M.F. of the new cells varies with the media employed: for

example, a platinum tube cell with calcium borate at nearly a white heat, E.M.F. = 0.36 Daniell, whilst a similar cell with a Berlin porcelain tube at nearly white heat = 0.7 Daniell. The current is arrested if there is not complete combustion in the source of heat applied to the cell, in fact, a reducing flame causes a reversal of the direction of the current. The platinum-hydrogen acts as a zinc element in an ordinary galvanic cell.

The following substances have been employed more or less successfully as media, glacial phosphoric acid, sulphuric acid (at boiling point only slight current), alkaline and alkaline earthy haloid salts, glass, and vitrified earthenware and porcelain. The use of the latter substances allowed the introduction of metals which for obvious reasons could not be employed with the above metallic salts. The following metals have been employed up to the present time:—Platinum, palladium, gold, iron, nickel, molybdenum, copper, and silver. Actual contact between the metals and media is essential, and therefore with glass the metal is placed inside a glass tube which is then fused on the metal (in the case of oxidisable metals a current of coal-gas is passed during the fusion), and while the glass is still soft, the exterior is covered with metal. For the finely divided metallic elements spongy platinum, or an alcoholic solution of platinum chloride, is painted on the glass which is then ignited, and a film of platinum is left on the glass, the conducting wire is put round in the form of a spiral, with other metals the oxide is put in the tube, and is subsequently reduced by hydrogen. Sulphates, carbonates, nitrates, and glass containing metallic oxides reducible by hydrogen are unsuitable as media for the present purpose.

The hydrogen is transmitted not only through the inner tube, but also through the intervening medium and external metallic cover. The amount of gas transmitted varies greatly with the nature of the media and the nature of the metallic layer; thus with the two,  $\frac{1}{100}$  inch thick platinum tubes, with a favourable medium, and 3.3 square inches of inner tube in contact with it, at nearly a white heat, 0.7 c.c. of hydrogen passed through per minute; with finely divided metal and soft glass medium, the hydrogen transmitted at a full red heat may be as high as 0.6 c.c. per square inch per minute, with Berlin porcelain it is only 0.2 c.c. per square inch per minute at white heat, and is less at red heat.

Gaseous mixtures containing free hydrogen give rise to currents, whilst carbonic oxide produces no electrical disturbance with iron or platinum. The galvanometer employed was one adapted for rather strong currents with small resistance; it was graduated by means of a voltmeter, and some of the deflections were of the following values in c.c. hydrogen per minute:—10°, 0.07; 20°, 0.21; 30°, 0.60; 40°, 1.35. Some cells may be constructed by nearly covering pieces of metallic (platinum, nickel, iron, copper) wire or rod with fused glass, the external coating being foil. On heating these in the oxidising flame, a current is produced which is due to the withdrawal of hydrogen from the inner core; when this current diminishes, the application of a flame containing free hydrogen immediately gives rise to a strong current in the reverse direction accompanied by the reabsorption of

hydrogen by the internal metal wire; a similar effect is produced if a platinum plate is suspended in a platinum tube containing fused glass (magnesium and calcium borates), when alternate electric currents may be produced by simply altering the nature of the flame. These effects can be repeated as often as required. The initial deflection produced by the "normal" or "reverse" current is  $18^{\circ}$  to  $20^{\circ}$ ; this falls within 10 to 15 minutes to nearly zero. When iron wire is completely covered with glass (except the conducting wire which is not heated), the oxidising flame deflection may gradually be brought actually to zero. Experiments have been made in which the inner platinum tube is connected with a Sprengel pump and immersed in fused glass in a platinum cell heated in the oxidising flame; under these circumstances a good vacuum could be pumped, and there is no deflection of the galvanometer, but as soon as a reducing flame is employed there is a steady deflection of  $15^{\circ}$ , and bubbles of hydrogen come down the fall tube of the pump, and in 15 minutes 1.33 c.c. were collected. Hydrogen could not be made to pass through a glass or porcelain tube either by means of oxygen or vacuum alone. When glass is fused in a platinum crucible over a gas flame, hydrogen can be seen forming and rising from the sides, especially from the hottest part, if the glass is allowed to become viscid by cooling, and the gas flame again applied, tubes like those mentioned above may be burst by the bubble of hydrogen formed on the inside of the tube. It is noteworthy that fused vitreous matters do not conduct electricity of low tension unless hydrogen is present. D. A. L.

**Weight Voltameter for Measuring Electric Currents.** By L. N. LEDINGHAM (*Chem. News*, 49, 85).

**Electrolysis of Dilute Sulphuric Acid and Hydrated Salts.** By J. H. GLADSTONE and A. TRIBE (*Chem. News*, 49, 61).—Frankland (Abstr., 1883, 839) suggests that in charging and discharging storage batteries one of the changes which occurs is the electrolysis of hexabasic sulphuric acid in accordance with the views of Bourgoin. The authors have made some experiments with 4.2 per cent. sulphuric acid; the apparatus employed consisted of a U-tube having a stopcock in the centre of the horizontal part. The hole in the stopcock was packed with asbestos in such a manner as to prevent both the mechanical admixture of the liquids in the two limbs, and also electrical endosmose. In experiments with currents of different densities it was observed that the increase of sulphuric acid in the positive compartment per equivalent of hydrogen set free decreased with the lowering of the current density. In other experiments with sulphate of copper in one limb and sulphuric acid in the other, it was found that the acid accumulated was largely in excess of the copper deposited, this being due to the *unequal transference of the ions*. From these results and from those of some previous investigators, the authors conclude that the electrolytic method is incapable of determining whether  $\text{H}_2\text{SO}_4$ , or a hydrate thereof, gives rise to the current, and moreover from other experiments with copper and zinc sulphates, in which both limbs of the U-tube were filled with the same solution,

they show that neither the composition nor even presence of a hydrated salt in aqueous solution can be determined by this method.

D. A. L.

**Absorption of an Iodine-compound by Aluminium.** By G. GORE (*Chem. News*, 49, 1—2).—When sheet aluminium is immersed in a colourless aqueous solution of iodic acid either alone or together with a piece of sheet platinum so as to form a voltaic couple, the liquid becomes discoloured, there is a copious evolution of gas from the aluminium, and the current produced, if utilised, causes a considerable deposition of silver from a plating solution. After three hours, the aluminium is considerably corroded, and even after repeated washing with cold and boiling water retains iodine, which cannot be extracted with carbon bisulphide.

In a quantitative experiment, a piece of aluminium two inches square and weighing 15·752 grains, was immersed in a solution of 25·749 grains of iodic acid in 5 ozs. of water, at a temperature of 16°. After three hours, 14·685 grains of metal remained undissolved, and 2·340 grains, apparently iodine, were absorbed by it. Only very slight absorption of iodine takes place when solutions of potassium iodide or iodate are electrolysed, using aluminium electrodes, or when sheet aluminium is immersed in aqueous hydriodic acid containing dissolved iodine. Whilst there is no absorption when a solution of sulphuric acid and iodide is electrolysed as above, neither is there absorption when aluminium is immersed in a cold saturated aqueous solution of iodine, nor in dilute hydrochloric acid containing iodine, nor in dilute sulphuric acid and potassium iodide. It is, therefore, inferred that the absorption only takes place with the nascent substance at the corroding surface of the aluminium.

The aluminium plates after action appear, under the microscope, to be partly disintegrated into thin layers.

D. A. L.

**Pyroelectric Properties of Boracite.** By K. MACK (*Wied. Ann.*, 21, 410—421).—The optical, thermic, and pyroelectric properties of boracite have been the subjects of a series of investigations by Haüy, Hankel (Abstr., 1883, 412, 546, 950), Mallard, Baumhauer, and others. This research is based upon an observation of Kundt that Lichtenberg's figures can be used for an examination of the pyroelectric properties of crystals.

The method of observation consisted in heating the crystal to be examined in an air-bath, removing it by a pair of pincers previously heated in the same bath. The crystal is then passed through an alcohol flame and placed on a slip of wood or paper, where it is dusted thoroughly with the ordinary mixture of sulphur and red lead. On cooling, the particles of these substances arrange themselves in definite lines, thus marking out the field of positive and negative electricity. The crystals examined were cubical, rhombic, dodecahedral, and tetrahedral, obtained from Stassfurt and Luneberg.

The general results of the investigation may be summed up as follows:—

(1.) The difference of potential, whether positive or negative, does

not extend over the whole surface of a crystal, but follows certain definite lines.

(2.) If upon a crystal, in which either the rhombic or dodecahedral form is dominant, there be conceived to be marked out a smaller, perfect rhombic dodecahedron, so that its principal crystallographic axes coincide with those of one or other of the above crystals, and there be projected from the common middle point, the angle of the latter dodecahedron upon the surface of the crystal, then a system of lines is obtained, coinciding with the lines of the electro-positive or -negative potential differences. Those lines which connect the middle points of smooth and glistening tetrahedral surfaces are coloured yellow, but those which lie symmetrically to any principal symmetrical plans of the regular system are red. This system of lines coincides with the optical system of lines of double refraction which have been described by Klein and Baum-hauer.

It would appear then that there is an intimate connection between the optical and pyroelectric properties of boracite. The former are probably conditioned by a state of tension of crystal, and the experiments of T. and P. Currie would seem to point to the same conditioning of the pyroelectricities.

V. H. V.

**Production of Low Temperatures by the Use of Liquefied Gases.** By CAILLETET (*Ann. Chim. Phys.* [5], 29, 153—164).—To remedy the inconveniences previously attending the use of Thilorier's apparatus for condensing gases, the author has devised certain improvements in the arrangements and fittings of the apparatus, by which the liquefaction of ethylene and other gases can now be effected without difficulty, although the pressure required may amount to several hundred atmospheres. As liquefied ethylene does not solidify at even the lowest known temperature, it has the important advantage over carbonic anhydride and nitrous oxide of remaining transparent during its volatilisation, and of thus permitting the effects on the substances immersed in it to be readily observed. The drops of liquid ethylene are allowed to pass with moderate velocity into a test-tube containing the substance, and this tube is concentrically enclosed in another glass vessel, the air in the intervening space being completely desiccated, so that no deposition of ice can take place on the cooled tube. The author has obtained by liquid ethylene a degree of cold indicated by  $-107^{\circ}$  on a sulphide of carbon thermometer.

R. R.

**A Convenient Temperature Regulator.** By W. T. RICHMOND (*Amer. Chem. J.*, 5, 287—289).

**Use of Mercury Thermometers, with particular Reference to the Determination of Melting and Boiling Points.** By J. M. CRAFTS (*Amer. Chem. J.*, 5, 307—338).

**Thermo-chemistry of Haloid Salts.** By BERTHELOT (*Ann. Chim. Phys.* [5], 29, 198—288).

In this series of eight papers the author, by adducing the data for



the application of his general theory to the case of the double haloid salts, adds a new chapter to the researches on chemical mechanics which he has pursued for so many years. A complete theory of saline reactions requires that *all* the compounds capable of being formed under the given conditions of the experiment shall be taken into account. Thus, the heats of formation and of dissociation, not only of the simple salts, but those also of all the acid, the basic, the double, the hydrated, and the anhydrous salts that can possibly be formed under the circumstances, must be determined beforehand. This has been done in many cases in the present series of papers, and the observed reactions explained by the principle of maximum work, as in the theory of chemical equilibrium already advanced in the author's *Essai de Mécanique chimique*. The first paper merely states the range of the investigation. The second gives the thermal data for double salts formed of mercury, of potassium, or of both, united with one or two of the three halogens, chlorine, bromine, iodine, or with their analogue, cyanogen. Some interesting particulars are noted concerning the successive physical and chemical changes of such salts. Thus, the heat of combination from the simple salts is very small, except when the iodide is one component, when the heat, reckoned from the yellow iodide, is about the same as that disengaged in the transformation of yellow to red iodide. The combination of potassium iodide with mercuric cyanide liberates much heat, and the author regards the resulting product as a triple salt formed by a union of mercuric iodide with a double cyanide of mercury and potassium.

In the third paper, it is shown that haloid salts of mercury, like those of other metals, combine with their corresponding hydracids, forming well-defined, crystallised acid salts. Red crystallised mercuric iodide dissolves readily in dilute hydriodic acid with disengagement of heat, and there is evidence of the stability of the compound thus formed, which may be regarded as mercurio-hydriodic acid, corresponding with a whole series of double salts, and analogous to the well-known complex acids derived from metallic cyanides. The heat of formation of acid chloride of mercury is less than that of the acid bromide, and much less than that of the acid iodide, whilst mercuric cyanide disengages scarcely any appreciable heat with hydrocyanic acid. The next paper treats of the heat of neutralisation of hydracids by the oxides of mercury and of potassium.

In the fifth paper are discussed the isomeric states of the haloid salts. The heat of transformation of 227 grams yellow mercuric iodide into red is 1.5 cal. In the formation of silver iodide by precipitation with potassium iodide, a succession of transformations occur in the amorphous state of the substance, and its passage from the last amorphous condition to the crystalline is not accompanied by any sensible thermic phenomenon, that is to say, the sum of the work done in the transformation is sensibly *nil*. The same thing happens when an organic substance passes into an isomeride of the same chemical functions. But when there is a change of condensation (polymerisation), or a change of chemical function with the same condensation, a notable disengagement of heat is usually observed.

The sixth paper is devoted to a study of the double decompositions of the haloid salts of mercury, and the numerical results confirm in all respects the author's principles. In all cases, the system which disengages the most heat is formed by preference whether as regards dissolved or insoluble substances, and Berthollet's laws are sometimes verified and sometimes quite contradicted, just as they are or are not in accordance with the thermochemical previsions.

The seventh and eighth papers deal with the haloid salts of silver, in the reactions of which there are certain special distinctive circumstances, such as the inverse displacements to which attention has lately been called. The author explains these by the formation of a double salt and the consequent separation of the alkaline salt along with the haloid salt in the solid form. The displacement of hydrochloric acid united to silver, by hydrobromic and hydriodic acids, whether free or combined with alkalis, takes place by reason of the thermic preponderance of these last acids, and would exclusively take place but for the existence of double and acid salts capable of giving rise to inverse reactions, which however are limited by the dissociation of the double salts. And with the silver salts, as with the mercuric, the whole resolves itself into one fundamental action, namely, that which corresponds with the thermic maximum.

R. R.

**Molecular Volumes of Salt Solutions.** By W. W. J. NICHOL (*Chem. News*, 49, 37).—In August, 1883, the author published (*Phil. Mag.*) results of experiments on molecular volumes of salt solutions of various strengths, wherein he found that in the case of ten potassium and sodium salts the difference in molecular volume of a solution, produced by the substitution of one metal for the other, or one radical for another, was in each case a constant quantity. The chlorides, sulphates, nitrates, chlorates, and hydroxides were examined. From the results, he inferred that the volumes of these elements and radicals, if determined in aqueous solutions and under similar conditions, are independent of the mode of combination; and, moreover, that when salts are dissolved in water the molecular interspaces in various solutions are nearly co-extensive. Recently these conclusions have received support from the results of Groshans (this vol., 143) and of Bender (*ibid.*, 144). Under these circumstances, the author now deduces the following law:—The volume of a metal in a salt, in dilute solutions (1 to 200 H<sub>2</sub>O), is independent of the non-metallic radical associated with it, and the volume of the radical is independent of the metal. The author has investigated the reactions between barium nitrate or chloride, and potassium or sodium sulphate, and finds that within certain limits the volume change is constant.

D. A. L.

**Some Convenient Quantitative Lecture Apparatus.** By A. MICHAEL (*Amer. Chem. J.*, 5, 353—359).

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## Inorganic Chemistry.

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**Atomic Weight of Oxygen.** By T. HILDITCH (*Chem. News*, **49**, 37—38).—In this paper, attention is drawn to the errors that may be encountered by using hydrogen prepared from zinc, or by diffusion of air through india-rubber connections, or by weighing the copper oxide in air, and the reduced copper in a vacuum or *vice versa*. The author then recommends the employment of electrolytic hydrogen purified by passing it over hot spongy platinum, and subsequently drying it with sulphuric acid or phosphoric anhydride in any future determination of the atomic weight of oxygen. D. A. L.

**Carbonic Anhydride in the Atmosphere.** By A. MÜNTZ and E. AUBIN (*Bied. Centr.*, 1883, 649).—Recent researches on the composition of the atmosphere have tended greatly to change the prevalent ideas on this point; this is especially the case as regards the carbonic anhydride in the air; for experiments have proved that the amount of this gas in the atmosphere is considerably lower (compare Abstr., 1883, 285, 614) than it was supposed to be, and, moreover, is subject to but slight variation. In order to inquire more completely into this matter, the authors took advantage of the Transit of Venus Expeditions; air was collected at the various stations in proper apparatus (Abstr., 1883, 121), and they now publish the results of the examination. The causes of variation are the different conditions of the sky and the force of the wind:—

	Vol. of CO <sub>2</sub> in 10,000 vols. of air.	
	Day samples.	Night samples.
Haïti .....	2·704	2·920
Florida .....	2·897	2·947
Martinique .....	2·735	2·850
Mexico.....	2·665	2·860
Santa Cruz (Patagonia) .....	2·664	2·670
Chubut (Patagonia) .....	2·790	3·120
Chili.....	2·665	2·820

It will be observed that these results differ but slightly from the numbers obtained for different places in France (North France, 2·962; neighbourhood of Vincennes, 2·54; the summit of Pic du Midi, 2·86). Calculated from the authors' results, the universal mean is 2·78; the mean for the northern hemisphere being 2·82, and that for the southern 2·71. It can therefore be assumed that the amount of carbonic anhydride in the air is lower in the southern than in the northern hemisphere: an assumption which finds support in the fact that the water is cooler in the former than in the latter hemisphere, and, according to Schlösing, there is a tension-equilibrium between carbonic anhydride in the sea and that in the air which is greatly influenced by temperature. D. A. L.

**Moist Phosphorus, Air, and Carbonic Oxide.** By A. R. LEEDS (*Chem. News*, **49**, 73).—In support of the author's results already communicated (this vol., 15), he refers to Baumann's contribution (*ibid.*), and in addition to the result given in the latter Abstract, quotes the following:—30 litres of air containing 2·45 litres of carbonic oxide yielded 64·6 mgrms. of carbonic anhydride, showing that 1·3 per cent. of the entire carbonic oxide was oxidised (comp. Remsen and Keiser, *ibid.*, 149). D. A. L.

**Dissociation of Brass.** By R. B. WARDER (*Chem. News*, **49**, 74).—A piece of brass wire, 150 mm. long and 1·43 mm. diameter, weighing 2·0570 grams, containing 36·02 per cent. of zinc, was heated to redness in a stream of hydrogen in a porcelain tube for several hours. The weight was taken from time to time, and it was observed that the rate of loss diminishes much more rapidly than the whole quantity of zinc present; for example:—

Hours.	Loss per hour.	Zinc present.	
1	0·1442	0·5967	
2	0·0601	0·5366	
3	0·0672	0·4694	
12	0·0095	0·3178	D. A. L.

**Combined Action of Potassium Dichromate and Chlorine on Ethyl Alcohol.** By GODEFROY (*Bull. Soc. Chim.* [2], **40**, 167—173).—When chlorine is passed into a mixture of ethyl alcohol and powdered potassium dichromate, a violent reaction takes place which converts the dichromate into a brown powder. If the action of the chlorine is continued beyond this stage, the brown compound disappears and is converted into a pink solid. The products at the end of the first stage of the decomposition are potassium chloride and an oxide of chromium of the composition  $\text{Cr}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , which is insoluble in dilute acids. This oxide is more easily obtained by the action of iodine on alcohol and potassium dichromate. It is a brown crystalline powder, which decomposes with incandescence at a red heat. At  $300^\circ$ , it slowly decomposes, losing water and oxygen, and passes into a black sesquioxide of chromium. At a red heat, the black sesquioxide is converted into the ordinary green variety.

The final inorganic products of the action of chlorine on alcohol and potassium dichromate are chlorides and oxychlorides of chromium, which have not yet been examined, and a double chloride of potassium and chromium,  $4\text{KCl} \cdot \text{Cr}_2\text{Cl}_6 \cdot \text{H}_2\text{O}$ . This substance exists as a red powder. When heated, it loses a molecule of water and turns blue. It is decomposed by solution in water, forming potassium chloride and chromium oxychloride.

The organic products of the reaction are aldehyde, ethyl chloride, acetic chloride, and ethyl acetate; a mixture of complicated chlorine derivatives is also formed towards the end of the operation.

W. C. W.

**A New Rhodium Salt.** By T. WILM (*Ber.*, **16**, 3033—3044).—The method by which the author obtained perfectly pure rhodium, chiefly from chloropurpurorhodium chloride, is fully described in the

first part of this paper. The pure metal (1·5 to 2 grams) was treated by Wöhler's method with sodium chloride and chlorine; part of the metal remained unattacked and part formed a red powder which was insoluble and probably an indifferent sesquichloride. The formation of the double salt is more easily effected by exposing the metal for some time to the air and afterwards igniting it in a current of hydrogen gas. The sodium chloride double salt was converted into the corresponding ammonium chloride salt, but owing to the quantity of sodium chloride present it was impossible to obtain good crystals until the sodium chloride had been precipitated by or crystallised out in presence of fuming hydrochloric acid.

From the solution of the ammonium chloride double salt, the two crystalline forms obtained by Claus were prepared:—No. 1,



in beautiful long four-sided columns from a solution containing little or no aqua regia, and No. 2,  $\text{Rh}_2\text{Cl}_6, 4\text{NH}_4\text{Cl}, 2\text{H}_2\text{O}$ , in octahedric, short, well-formed pyramids from the same solution by allowing it to stand or evaporating quickly with heat. If, however, the solution contains large quantities of aqua regia and a slight excess of ammonium chloride, the new salt crystallises out in raspberry-red flat crystals which, examined microscopically, are found to consist of regular six-sided plates, and have the formula  $\text{Rh}_2\text{Cl}_6, 8\text{NH}_4\text{Cl}, 7\text{H}_2\text{O}$ . The author has confirmed his results by again carefully preparing this salt from the purified metal, as the formation of a salt containing less chlorine in presence of excess of aqua regia was unexpected. This new salt was also prepared from salts No. 1 and No. 2 by warming them in excess of aqua regia and sufficient ammonium chloride—the change in colour and crystalline form being very distinct. By dissolving the new salt in water, a solution is obtained which at first has a raspberry-red colour, but on standing or, more quickly, on heating, it changes first into the red colour of No. 1 salt, and finally into the yellowish-red colour of No. 2. This solution can be converted again into the new form by treatment with excess of aqua regia and ammonium chloride.

A. B.

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## Mineralogical Chemistry.

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**Minerals from Lehigh Co.** By E. F. SMITH (*Amer. Chem. J.*, 5, 272—279).—*Allophane* from Allentown, near Balliettsville; mamillary and stalactitic incrustations, with mother-of-pearl appearance, coating pockets in the iron ore:—

H <sub>2</sub> O.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaCO <sub>3</sub> and MgCO <sub>3</sub> .	
40·86	21·39	35·20	1·96	= 99·41.

*Fluorite*, finely coloured, in limestone, near the above locality.

*Zircon* in minute crystals in loose quartz fragments; locality, near Macungie. Very fine specimens of *wavellite* are also found near this locality, as is also decomposed *wavellite*.

*Corundum* from Shimersville, in very fine gray and red crystals, containing  $\text{Al}_2\text{O}_3$  85.75, and  $\text{Fe}_2\text{O}_3$  4.26 per cent.

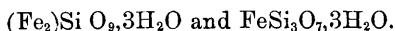
*Tourmaline* occurs in several localities. *Garnet* also often occurs, sometimes in large quantity and of various colours and degrees of translucency. *Stilbite*, from Hosensack. *Pyrolusite*, in crystals upon the inside of limonite nodules from Lehigh mountain. A little west of this locality *chloropal* is found, of an olive or greenish-yellow colour; no trace of crystallisation is present; it is decomposed completely by hydrochloric acid.

The following analyses are given:—(1.) Yellow; (2.) Dark yellow; (3.) Greenish-yellow; (4.) Yellowish-green; (5.) Yellowish-green; (6.) Light yellow; (7.) Brownish-yellow; (8.) Brownish-yellow; (9.) Brownish-yellow; (10.) Brown; (11.) Yellowish-brown; (12.) Specimen almost white:—

	$\text{H}_2\text{O}$ .	$\text{SiO}_2$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{P}_2\text{O}_5$ .
(1.) ..	19.61	40.20	39.52	0.40	trace
(2.) ..	19.79	40.81	39.30	—	—
(3.) ..	18.65	42.31	38.18	trace	—
(4.) ..	20.79	41.16	30.79	0.21	—
(5.) ..	20.45	41.41	35.35	—	—
(6.) ..	19.09	42.79	39.19	—	—
(7.) ..	19.27	42.37	38.17	trace	—
(8.) ..	19.31	41.35	39.09	—	—
(9.) ..	19.31	41.13	38.97	—	trace
(10.) ..	17.71	43.54	39.52	—	—
(11.) ..	19.36	43.00	37.50	—	—
(12.) ..	17.65	44.52	11.04	—	—

	$\text{MgO}$ .	$\text{K}_2\text{O}$ .	$\text{Al}_2\text{O}_3$ .	
(1.) ..	trace	trace	—	= 99.53
(2.) ..	—	—	—	= 99.90
(3.) ..	—	—	—	= 99.14
(4.) ..	—	4.54	2.05	= 99.54
(5.) ..	—	—	3.04	= 100.25
(6.) ..	—	—	—	= 101.05
(7.) ..	—	—	—	= 99.83
(8.) ..	—	—	—	= 99.75
(9.) ..	—	—	—	= 99.41
(10.) ..	—	—	—	= 100.77
(11.) ..	—	—	—	= 99.86
(12.) ..	trace	0.94	25.95	= 100.10

*Note*.—These numbers give the ratio  $\text{H}_2\text{O} : \text{SiO}_2 : \text{Fe}_2\text{O}_3 = 4.3 : 3 : 1$ , i.e., nearly those given by Naumann for nontronite,  $5 : 3 : 1$ , but quite different from the formulæ proposed for chloropal, viz.,



H. B.

**Minerals from Berks Co., Pa.** By D. B. BRUNNER and E. F. SMITH (*Amer. Chem. J.*, **5**, 279—281).—*Stilbite*, from Wheatfield mines. *Deweylite*, from Ruth's mine; whitish and brownish resinous coatings upon aragonite and with serpentine:—

H <sub>2</sub> O.	SiO <sub>2</sub> .	F <sub>2</sub> O <sub>3</sub> .	MgO.	CaO.	
19·49	45·65	0·20	34·38	trace	= 99·69
19·03	42·34	1·39	36·77	trace	= 99·53

*Vesuvianite*, from Fritz Island; was previously supposed to be garnet.

*Titanite*.—*Brucite* in distinct crystalline forms upon a dolomitic rock, near Reading in Fritz Island; also found near Sinking Spring, Spring Township. H. B.

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## Organic Chemistry.

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**Reactions of Tellurium.** By E. DEMARÇAY (*Bull. Soc. Chim.*, **40**, 99—100).—The tellurides are generally supposed to form reddish-violet solutions; but it is pointed out in this paper that this colour is due either to the presence of polytellurides or to some suboxide of tellurium. For if an alkaline solution of a telluride be boiled for some time with a reducing agent, such as phosphorus or aluminium, the violet colour disappears to reappear on contact with air.

The best process of obtaining methyl or ethyl telluride consists in warming at a temperature of about 80° the iodides of the corresponding hydrocarbon with finely-powdered tellurium. Dimethyl or ethyl tellurium diiodide is formed, from which the other derivatives can be obtained.

V. H. V.

**Decomposition of Chlorotribromopropionic Acid by Alkaline Hydroxides.** By C. F. MABERY (*Amer. Chem. J.*, **5**, 255—256).—This acid is completely decomposed if heated with baryta-water,  $(C_3HClBr_3O_2)_2Ba = C_2HClBr_2 + BaBr_2 + 2CO_2$ ; the distillate collected in bromine-water yielded  $C_2HClBr_4$ , melting at 33°, and therefore probably identical with chlorotetrabromomethane melting at 32—33°, prepared by Wallach and Bischof by the decomposition of  $\beta$ -dichloracrylic acid and treatment of the chloracetylene obtained with bromine.

By the action of alcoholic potash solution on chlorotribromopropionic acid, which is probably expressed by  $CBr_2Cl.CHBr.COOH$ , a small quantity of tribromacrylic acid is formed.

H. B.

**Substituted Acrylic and Propionic Acids.** By C. F. MABERY and F. C. ROBINSON (*Amer. Chem. J.*, **5**, 251—255).— $\beta$ -Dibromacrylic acid, unlike the isomeric  $\alpha$ -acid, will not unite with bromine at ordi-

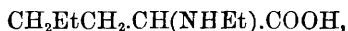
nary temperatures. At 100°, with pure bromine, union takes place easily, with production of *tetrabromopropionic acid*. This acid may be crystallised from carbon bisulphide or water, and melts at 118—120°. The barium, calcium, and potassium salts were prepared, and found to contain respectively,  $\frac{1}{2}$ , 1, and 2 mols. H<sub>2</sub>O. The barium salt heated in aqueous solution or distilled with baryta-water is decomposed:— $\text{Ba}(\text{C}_3\text{HBr}_4\text{O}_2)_2 = 2\text{C}_2\text{HBr}_3 + \text{BaBr}_2 + 2\text{CO}_2$ ; the distillate absorbed in bromine-water yielded pentabromomethane. When treated with an alcoholic potash solution, tribromacrylic acid is formed.  $\beta$ -Dibromacrylic acid is probably  $\text{CBr}_2 : \text{CH}.\text{COH}$ .

Chlorine acts like bromine on  $\beta$ -dibromacrylic acid; hydrobromic acid acts only very partially.

Bromine monochloride acts on bromopropiolic acid, but pure preparations could not be obtained; chloroform saturated with chlorine yields bromodichloracrylic acid. H. B.

**Amidated Acids of  $\alpha$ -Caproic Acid.** By E. DUVILLIER (*Ann. Chim. Phys.* [5], **29**, 164—178).—Amido- $\alpha$ -caproic acid was obtained by Hufner (*Zeits. f. Chem.* [2], **4**, 166); methylamidoacetic acid (sarcosine) by Liebig (*Annalen*, **62**, 310); methylamido- $\alpha$ -propionic acid, by Lindenberg (*J. pr. Chem.*, **70**, 244); and methylamido- $\alpha$ -butyric acid by the author (*Ann. Chim. Phys.* [3], **20**, 188). The latter has now obtained another homologue of the series, viz., methylamido- $\alpha$ -caproic acid,  $\text{CH}_2\text{Me}.\text{CH}_2.\text{CH}(\text{NH}.\text{Me}).\text{COOH}$ , by acting on pure methylamine with  $\alpha$ -bromocaproic acid prepared with caproic acid, obtained during butyric fermentation. The acid is white, crystalline, and soft to the touch; soluble in water and in boiling alcohol, but not in ether. The aqueous solution is neutral, and of a bitter taste; it does not give any precipitate with silver or mercurous nitrate. The preparation and properties of the sulphate, hydrochloride, platinochloride, and aurochloride, and also the cupric salt, are described at length in the paper.

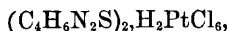
By acting on ethylamine with  $\alpha$ -bromocaproic acid, the author has in like manner obtained ethylamido- $\alpha$ -caproic acid,



a homologue of the already known ethylamido-acetic and ethylamido- $\alpha$ -butyric acids. Its properties closely resemble those of the corresponding methyl compound, and similar metallic and acid derivatives of it have been formed and examined. R. R.

**Propimine Thiocyanate.** By J. TSCHERNIAC and T. H. NORTON (*Amer. Chem. J.*, **5**, 227—231).—By the action of ammonium thiocyanate on monochloracetone, ammonium chloride and acetone thiocyanate are formed, which latter by the further action of ammonium thiocyanate is converted into the thiocyanate of propimine thiocyanate,  $\text{CH}_2(\text{SCN}).\text{CMe} : \text{NH}_2.\text{SCN}$ , with elimination of water. The salt thus obtained forms large crystals melting at 114—115°, soluble in alcohol and water from which it readily crystallises. By adding concentrated potash solution to these crystals, extracting with ether, and evaporating on a water-bath, an oily liquid is obtained; this is the

free base, propimine thiocyanate. It is obtained pure by distillation in a vacuum, boiling at 30 or 40 cm. at 136°, and at 760 mm. at about 232°; it forms a colourless crystalline mass melting at 42°. It is very soluble in water, and the solution has an alkaline reaction. By treating the thiocyanate of the base with silver nitrate or sulphate, the nitrate,  $C_4H_6N_2S.HNO_3$ , and the sulphate,  $C_4H_6N_2S.H_2SO_4 + 2H_2O$ , both crystalline salts, are obtained. On adding platinic chloride to a solution of the base in hydrochloric acid, the salt,



is precipitated. The free base heated with acetic anhydride yields acetyl-propimine thiocyanate,  $CH_2(SCN).CMe : NAc$ , a crystalline solid melting at 134°. Methyl iodide heated with the free base unites with it violently to form hydriodide of methyl-propimine thiocyanate,  $CH_2(SCN).CMe : NMeHI$ , crystallising from water in scales melting at 159.5°.

H. B.

**Parabromobenzyl Compounds.** By C. L. JACKSON and G. T. HARTSHORN (*Amer. Chem. J.*, **5**, 264—269).—The corresponding chlorine compounds have been previously described.

*Parabromobenzylsulphonic acid.*—The potassium salt was obtained by heating potassium sulphite with parabromobenzyl bromide; it is crystalline and anhydrous. By precipitation with lead acetate, and decomposition of the precipitated lead salt by sulphuretted hydrogen, the free acid was obtained, and thence the pure calcium, barium, and lead salts; the barium salt contains 1 mol.  $H_2O$ . On treating the potassium salt with phosphorus pentachloride, the chloride of the acid was obtained; it is crystalline, and melts at 115°.

*Parabromobenzyl sulphide* is easily formed by the action of sodium sulphide in alcoholic solution on parabromobenzyl bromide; it forms large crystals melting at 59°. If treated with chromic acid in acetic acid solution, it is oxidised to parabromobenzylsulphone.

The *parabromobenzyl mercaptan* was made by the action of an alcoholic solution of potassium sulphhydrate on the parabromobenzyl bromide, and precipitation with water; it melts at about 25°, and by the action of the air soon changes into the bisulphide; mercury parabromobenzyl mercaptide is formed by the action of mercuric oxide and water on the mercaptan; it crystallises easily. Parabromobenzyl bisulphide was prepared by the action of air on the mercaptan, and also directly from sodium bisulphide and the bromide; it is crystalline, and melts at 87—88°.

H. B.

**Some Reductions with Zinc and Ammonia.** By W. G. MIXTER (*Amer. Chem. J.*, **5**, 282—286).—In a previous paper (*Amer. Chem. J.*, **5**, 1) the author described the reduction of nitracetanilide; parazoxy-acetanilide crystallised out, and the filtrate contained *parazoacetanilide*; it is now shown that a large amount of paraphenylenediamine is also formed, and may be removed from the dried residue by very dilute hydrochloric acid.

Parazoacetanilide treated with hot concentrated hydrochloric acid yields the hydrochloride of a base, which is also formed by saponifica-

tion. Analysis showed the base to be *parazoaniline*. It unites with 2 mols. HCl, and nascent hydrogen converts it into paraphenylenediamine, hence its formula is  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ ; it melts at  $235-240^\circ$ . Chrysoïdine melts at  $110^\circ$ , and yields with nascent hydrogen aniline and triamidobenzene, hence the constitution of this isomeride is  $\text{C}_6\text{H}_5\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_3(\text{NH}_2)_2$ . Attempts have been previously made to prepare parazoaniline by reducing paranitraniline, but the hydrazo-compound alone was obtained.

*Parazoxybenzanilide* has been prepared in a manner similar to the meta-derivative (previous paper), viz., by reduction of paranitrobenzanilide. It is pure yellow, and melts at  $310^\circ$ . The azo-compound does not appear to be simultaneously formed; amidobenzanilide is formed, and a large quantity of the nitro-compound remains unacted on.

*Azoxybenzotoluide*.—Nitrotoluidine, melting at  $77.5^\circ$ , was treated with benzoic chloride, and the nitrobenzotoluide reduced with zinc and ammonia; the product melts at  $290^\circ$ , and is insoluble in water and alcohol. Attempts to replace the benzoyl group by hydrogen were unsuccessful.

The azoacetanilide and azoaniline complete the analogy indicated in the former paper between the reduction-products of nitrobenzene and those of paranitracetanilide, with the exception that no hydrazobenzene or benzidine analogue has as yet been obtained. The meta-oxybenzanilide is the only meta-compound of the series investigated; no results have been obtained with ortho-derivatives. The use of zinc and ammonia seems to possess considerable advantages as a reducing agent; probably sodium-amalgam with a large excess of ammonium chloride would act in the same way. H. B.

**Method of Preparing Borneol from Camphor.** By C. L. JACKSON and A. E. MENKE (*Amer. Chem. J.*, 5, 270—271).—The camphor is dissolved in 10 parts of alcohol, a small excess of sodium gradually added, and the alcohol distilled off; water precipitates crude borneol. After washing with water it is crystallised from alcohol. The reaction is expressed:  $\text{C}_{10}\text{H}_{16}\text{O} + \text{H}_2 = \text{C}_{10}\text{H}_{18}\text{O}$ ; the yield is excellent, 94 per cent. of the theoretical amount being obtained.

H. B.

**Constitution of Chlorophyll.** By E. SCHUNCK (*Chem. News*, 49, 2).—The author extracts leaves with boiling alcohol, and after some time filters; the filtrate is mixed with its own volume of ether and two volumes of water; it then forms two layers, which are separated. The lower layer is yellow, and reduces Fehling's solution. The upper layer is green, and contains all the chlorophyll; it is thoroughly washed free from everything soluble in water. When the ether is evaporated the bright green residue, dissolved in alcohol and treated with alcoholic potash, does not reduce Fehling's solution, but if it is previously treated with concentrated sulphuric acid in the cold, or if its alcoholic solution is boiled with hydrochloric or sulphuric acid, the alcohol driven off, the residue treated with water, filtered, and the filtrate made alkaline, mixed with Fehling's solution and boiled, the usual glucose reaction is obtained. The glucose or glucose-like sub-

stance is a pale-yellow gummy compound. The author, therefore, concludes that chlorophyll is either a glucoside or is associated with a glucoside (compare Tschirch, *Trans.*, 1884, 57—62).. D. A. L.

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## Physiological Chemistry.

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**Development and Nutrition of Japanese Silkworms (*Bombyx Mori*).** By O. KELLNER (*Landw. Versuchs.-Stat.*, **30**, 59—86).—The rearing of the larger agricultural animals, such as the cow and horse, is not much attended to in Japan, but the cultivation of the silkworm and of the mulberry trees needed for its food has been a favourite industry for ages; the tendency of the people to excel in smaller industries rather than larger has brought everything connected with silkworm culture to a high state of perfection.

The author refers to the researches of Peligot as the principal contribution to a knowledge of the chemical constitution and food assimilation of the worm, but his investigations left very numerous questions unsolved, which the author, living at the oldest seat of the industry, has endeavoured to answer.

A number of worms were taken after hatching, and fed with weighed and analysed food, the worms being analysed at certain periods, four of which were the periods of casting their skins, when they cease to feed, and the intestine is empty; 5th period, when they were ready to spin; 6th, when the pupa becomes hard in the cocoon, and the butterfly as it leaves the cocoon; the excrement, when large enough to be removed, was examined by itself. The variety is very hardy, as out of 13,916 but 19 worms died in course of the experiments, whilst in European silkworm culture the average loss is 15 per cent.

The mulberry trees are cultivated somewhat like our basket willows, cut back, and the yearling shoots only used. The analyses are given very fully in tabular form and minute detail, some of which are of interest. It appears that the silkworm is unable to digest the fibrous portion of the leaves. Albumin and fat were digested to an amount not exceeded by ruminants; non-albuminous nitrogenous substances appear to be but slightly absorbed.

Table A contains the chemical analyses of the worms in their different stages, of the empty cocoon, the pupa, and the butterfly. It will be seen that the insect contains a very large proportion of water, which gradually increases until it is ready for the cocoon.

Table B shows the increase of weight of the worm, which is enormous. When ready to spin it has increased its living weight 5400 times.

TABLE A.

	Newly hatched worms.	Periods.					Empty cocoon.	Pupa.	Butterfly.
		1.	2.	3.	4.	5.			
In fresh insect—									
Water .....	75·94	84·10	85·68	86·92	87·81	80·33	12·50	78·89	71·77
Dry substance.	24·06	15·90	14·32	13·08	12·19	19·66	87·50	21·10	28·23
In 100 parts dry substance—									
Protein, less	75·58	75·42	73·26	72·52	72·23	59·16	98·82	55·81	56·58
chitin....			5·32	5·46	5·40	4·77	—	3·89	7·38
Chitin ....									
Fat.....	16·20	8·72	10·73	12·95	11·47	16·31	0·01	28·17	32·01
Ash .....	6·40	9·05	8·98	9·48	9·32	6·06	1·18	5·62	3·94
Unestimated..	1·82	6·81	1·79	—	1·58	13·70	—	6·51	0·10
Total nitrogen ..	12·09	12·07	12·04	11·93	11·88	9·75	17·97	9·16	9·49
Albumin and	11·39	11·06	10·42	9·81	9·94	8·11	—	5·68	8·18
peptone N..			0·32	0·33	0·32	0·29	—	0·23	0·44
N in chitin ..									
N uncombined ..	0·71	1·01	1·30	1·79	1·62	1·35	—	3·25	0·87
N per cent. of total .....	5·8	8·3	10·80	15·0	13·3	13·8	—	35·5	9·2

TABLE B.

	Live weight.	Dry weight.	Proportion of living weight to freshly hatched worm.	Proportion of dry weight to freshly hatched worm.
Freshly hatched.....	0·414	0·098	1·0	1·0
Period 1 .....	4·734	0·752	11·4	7·7
„ 2 .....	25·570	3·662	61·8	37·4
„ 3 .....	114·050	14·920	275·5	152·2
„ 4 .....	514·170	62·690	1241·9	639·7
„ 5 .....	2220·990	436·850	5364·7	4457·7
Empty cocoon .....	140·000	122·500	—	—
Pupa minus cocoon .....	1030·000	217·410	—	—
Pupa and cocoon .....	1170·000	339·910	2826·1	3468·5
Butterfly .....	503·560	142·170	1215·0	1450·7

J. F.

**Influence of Cotton-seed Cake on the Secretion of Milk.**—By M. SIEWERT (*Landw. Versuchs.-Stat.*, 30, 145—160).—Cotton-seed cake made from whole seeds has lately been used in England for feeding cattle in place of linseed cake, and with good results: the cake which finds its way into Germany has, however, up to the present been made from the shelled seeds, and has been described as injurious when given to young cattle, although this may be due to the high concentration of the contained nutriment. To obtain exact information on the nutritive qualities of the two kinds of cake, experiments were instituted at various farms in the north of Germany, specially with a view of ascertaining the influence of the cake on the production of milk. Out of eight series of experiments, six agreed in the result that the quantity of milk decreased, while the percentage of sugar was raised at the expense of the other solid constituents, independently whether whole or shelled seed cake was used. The favourable report of English consumers was probably based on the fattening qualities of the cake.

J. K. C.

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## Chemistry of Vegetable Physiology and Agriculture.

**Function of Silica in the Growth of Maize.** By V. JODIN (*Ann. Agronomiques*, 9, 385—392).—A grain of maize was submitted to water culture in 1875 in a solution containing suitable proportions of nitric, phosphoric, hydrochloric, and sulphuric acids, potash, soda, lime, magnesia, and ferric oxide, but as free as possible from traces of silica. A grain from the crop obtained was sown in a similar solution in 1876, and yielded a plant and seeds with which the experiment

	Ash constituents per cent. of entire dry crops obtained from					
	Soil culture, 1875.	1st water culture, 1875.	2nd water culture, 1876.	3rd water culture, 1877.	4th water culture, 1881.	3rd water culture, sown in soil, 1881.
P <sub>2</sub> O <sub>5</sub> .....	0·75	0·19	0·38	Not analysed.	0·66	0·63
HCl.....	0·38	0·16	0·09		0·46	0·27
SO <sub>3</sub> .....	0·26	0·22	0·14		0·48	0·11
SiO <sub>2</sub> .....	3·27	0·04	0·20		0·17	1·85
K <sub>2</sub> O.....	3·65	1·74	1·80		4·42	0·57
Na <sub>2</sub> O.....	0·22	0·15	0·09		0·72	0·25
CaO.....	1·18	0·98	0·96		0·69	0·76
MgO.....	0·10	0·12	0·12		0·36	0·32
Fe <sub>2</sub> O <sub>3</sub> .....	0·05	0·08	0·05	Not analysed.	0·10	traces
CO <sub>2</sub> and loss.....	4·04	1·12	0·83		1·59	0·03
	13·90	4·80	4·64	6·00	9·65	4·79

was repeated in 1877. This time also a crop was obtained, a seed of which was sown in 1881, yielding a plant the seeds of which did not come to maturity. Another seed of the third generation (1877), however, when sown in only 82 grams of garden soil, and watered with the mineral solution, yielded an abundant crop with 24 ripe grains, so that the seeds had by no means lost their fertility by the three successive cultivations in a liquid deprived of silica. The effect of this cultivation on the mineral constituents of the plant, as compared with plants grown normally in soil, is shown by the appended ash analysis (p. 669).

The most striking point is the feeble mineralisation of the plants from the seed of the 3rd generation of water-culture sown in soil, although watered with an abundant supply of minerals. It contained less than one-sixth the normal proportion of potash, but recovered something like the original proportion of silica. The facts accord with Déhérain's conclusion that a large proportion of the mineral constituents of plants is not assimilated because essential to plant growth, but is deposited in the tissues of the plant as bye-products or residues of the various physical and chemical processes of growth.

J. M. H. M.

**Nature of the Gases contained in Vegetable Tissues.** By J. BOEHM (*Ann. Agronomiques*, 9, 418—422; from *Bot. Zeit.*, 1883, Nos. 32, 33, 34).—The author's experiments have been made by exhausting cylinders of cork and wood with a mercury pump, and submitting the extracted gases to analysis.

*Cork*, whether in its natural condition or after desiccation, yields gas containing 25 to 34 per cent. of oxygen; when the cork is dried at 100° a little carbonic anhydride is found.

Cylinders turned out of the dead heart-wood also yield gas rich in oxygen, but if the exhaustion is continued for some time at the ordinary temperature of the air, the oxygen becomes gradually replaced by carbonic anhydride.

Cylinders of mahogany prepared from heart-wood, sap-wood, and from a small branch, were examined immediately after preparation; again after drying in the air for a year; and again after a further desiccation over sulphuric acid and potash. When they were freshly prepared, the percentage of oxygen ranged from 4.83 to 16.40; in the dried samples, it rose to 24.29 to 34.40.

The author ascribes this richness in oxygen to the fact that oxygen traverses cellular membranes more freely than nitrogen. The substance of the cells themselves appears to have no power of absorbing or condensing oxygen.

J. M. H. M.

**Contributions to a Knowledge of Chemical Processes in the Plant.** By A. EMMERLING (*Landw. Versuchs.-Stat.*, 30, 109—144).—In a previous paper (*ibid.*, 17, 161) it was shown that oxalic acid decomposes calcium nitrate, with formation of crystallised calcium oxalate and free nitric acid. This reaction was made use of by Holzner in explaining the existence of calcium oxalate in plant cells, and he further considered the oxalic acid to be a decomposition-product of albumin. De Vries, on the contrary, supposes the oxalate of

lime to be merely the form in which superfluous lime is separated from the sap, and occurs when the plant is situated in a soil very rich in lime. Holzner's hypothesis, however, finds confirmation in the chemical reactions known to occur when oxalic acid is brought into contact with any salt of lime, and gives the most simple explanation of the frequent occurrence of calcium oxalate in the plant.

In the further pursuance of this investigation, the author has endeavoured to determine the action of oxalic acid on potassium nitrate. A qualitative result had been previously obtained by means of diffusion, but to determine the exact amount of decomposition, the action of various mixtures of oxalic acid and potassium nitrate or nitric acid on marble plates was the method employed. The action of nitric acid alone in various degrees of dilution was studied, and this was found to vary directly with the quantity of nitric acid in solution, and the temperature employed, whereas oxalic acid alone reacts but very slightly, as the marble quickly becomes covered with an impenetrable coat of calcium oxalate, which prevents further action. The addition, however, of a small quantity of nitric acid alters this completely, a lively and continuous reaction setting in, and lasting as long as any unsaturated acid remains. 1 gram-mol.  $\text{HNO}_3$  in 1004 litres water dissolved 70 mgrms. calcium carbonate in 72 hours, whilst 1 mol. nitric acid with 25 mols. oxalic acid in the same quantity of water dissolved 1180 mgrms. in 72 hours. The reaction takes place in two stages, calcium nitrate being first formed, which is decomposed into calcium oxalate and free nitric acid, the latter beginning its action again. The quantity of nitric acid must not, however, be too small, 25 mols. of oxalic to 1 of nitric acid being the limit beyond which it is not possible to go without disturbing the rapidity of the reaction.

The effect of nitric acid alone decreases with the time it has been in contact with the marble, so that its action during any given part of the time could be calculated, and was found to agree fairly well with the practical results of experiment.

The experiments with mixtures of nitric and oxalic acids in various proportions and dilutions showed that generally speaking the action of such a mixture is, *cæteris paribus*, proportional to the sum of the molecules of both acids in the volume-unit of liquid. This law, however, holds good only between certain limits; as mentioned above, the quantity of nitric acid must not be too small, and it must likewise not greatly exceed the amount of oxalic acid present, as a mixture of even equal parts of the two acids is never equal in its action to nitric acid alone, owing to the mechanical hindrance effected by the formation of crusts of calcium oxalate on the marble plate, which only after a time fall off.

Mixtures of oxalic acid and potassium nitrate were used in the same proportions as those of the two acids, and it was found that the quantity of potassium nitrate remaining constant, the action varied directly with the amount of oxalic acid when the concentration was not too great. In other words, oxalic acid and potassium nitrate act like a mixture of the two acids on calcium carbonate. This fact,

however, gave no light as to the amount of potassium nitrate decomposed by oxalic acid under various conditions, but by use of the numbers given by Thomsen for the proportions of the avidities of acids for bases, the author arrives at a formula for the determination of this coefficient, and finds it to vary from 54 to 14 per cent., as the potassium nitrate is present in proportions of 0.1 to 2 mols. to 1 of oxalic acid.

The above experiments show clearly that oxalic acid attacks potassium nitrate with formation of free nitric acid, and that the presence of a small quantity of the latter is sufficient to produce a continuous action of oxalic acid on calcium carbonate. In certain cases, true rhaphidic crystals of calcium oxalate were obtained. J. K. C.

**The Sum of Mean Temperatures in Relation to the Cultivation of Corn and Maize.** By F. SESTINI and A. FUNARO (*Landw. Versuchs.-Stat.*, **30**, 97—108).—Some previous experimenters on this subject have stated that a certain sum of mean temperatures is necessary to the ripening of various kinds of corn: the total amount, however, varies with the climate, and in northern countries is less than is necessary further south. In the growth of maize, for instance, the observed totals of mean temperatures vary from 2463 to 3163°, and further observations might lead to even greater differences. The authors' own experiments were arranged as follows:—Three small plots of land were planted in the usual manner with maize; Plot A was covered with a tent of white calico, B with black, and C was left open: the temperatures of the soil and air were carefully observed the whole time in each of the three experiments, and the condition of the plants also noted from time to time.

The plants in B were weak, and died off in the middle of July, while those in A grew faster than any of the others, and gave a much larger yield than those in the open (30 kilos. against 26.3). Analysis, however, showed that the quality of the former was very much inferior to that of the latter. The sum of mean temperatures did not vary greatly in either of the three cases. A was, however, in this respect slightly superior to C, but the difference was not sufficient to account for the considerable variation in the yields obtained, and this shows that the quantity of heat supplied was only one factor in the conditions governing the growth of the plant. J. K. C.

**Rice Culture in Japan.** By O. KELLNER and J. SAWANO (*Landw. Versuchs.-Stat.*, **30**, 18—41).—The many varieties of rice grown in Japan may be classed in two groups—mountain rice and marsh rice; the former thrives on dry soil, and perishes when sown in the wet rice valleys, where the second flourishes, to die in its turn if sown on dry soil. The two classes are morphologically the same, and the cause of this great difference is yet undiscovered. The general mode of rice culture is as follows:—The seed for the next year's sowing is selected before the plants are cut, the best developed ears are chosen, and the fullest grains struck out by hand, sorted by throwing them into water, and dried by being packed in straw and hung up in a dry airy place. When the time of sowing arrives, the seeds are steeped in water

until they swell, an average of about ten days; they are then spread on mats in the sun during the day, removed to the house at night, and covered. After about five days the plumule appears; in cold localities the seeds are often watered with tepid water, or even buried in the compost heap. The seed-bed is now carefully dug, and worked until it is a fine slimy mud. When the plumules are about 6 mm. long, the seeds are sown broadcast in it, the water is let on during the nights, and turned off during the day, that the seeds may be protected from frosts at night, and get the full benefit of the warmth of the sun in the day; in 40 to 56 days the young plants have attained a height of 18 to 24 cm., and are then transplanted to the field, previously well dug, and manured with green or other available manures; the plants are put in tufts or bunches equidistant, varying according to the fertility of the soil. The irrigation of the growing crop is a most trying operation, manual labour only being employed; the removal of weeds also requires constant care. The period of blooming is a very critical and anxious one for the farmer; wind and damp are both injurious. The harvest lasts from the end of September to the end of November, and the grain is cut with the sickle; the yield varies with the quality of the land, and for all Japan averages 27.3 hectolitres per hectare. The authors experimented in three directions:—

1. Culture in water, in order to find whether the marsh rice draws its supply of nitrogen from ammoniacal compounds or from nitrates.

2. On the process of nitrification in rice-fields.

3. On the composition of the irrigation-water before and after use.

The water culture was carried out in pots filled with carefully washed sea-sand, and, except for some hours each afternoon, they were covered up with distilled water; when the experimental solutions were applied, matters were so arranged that the rootlets touched their surface.

The solutions of nitrates and ammonium compounds were so arranged that each contained equal amounts of nutritive material. The authors give in tabular form analyses of the plants in different stages of their growth, and observations on the appearance of the plants, from which they draw the conclusions that the rice plant can supply itself with nitrogen equally well from dilute solutions either of nitrates or of ammonium compounds, when one class of bodies only is present with the necessary mineral constituents. Solutions containing nitrates only, cause a very slow progress in the first few weeks of the plant's life, afterwards the growth is normal. Ammoniacal solutions on the contrary, stimulate early growth, and do not act so favourably in the later periods, which makes the authors think manures for rice should contain nitrogen in both forms.

Experiments on nitrification of the soil of rice-fields under water were made, but without satisfactory results.

The examination of the water before and after use in irrigation was the next subject of investigation. The whole time of irrigation was divided into three periods, and the water daily examined with such precautions as the authors thought necessary so as to avoid error.

The outflowing waters were found poorer in mineral matters than

when they were let in on the field; a portion was undoubtedly directly taken up by the plants, and another portion retained by the soil; the greatest loss was in nitric acid, while the ammonia was much higher in the outflowing water, the probable reason being that it was very low in ammonia on entering the field, or it might be that the water dissolved some of the ammoniacal compounds in the soil, the loss of nitric acid may have had some influence on the increase of ammonia. The authors consider that relative proportions of nutritive matter in the water at entrance and exit depends on such a number of varying conditions that further experiments are desirable.

On an occasion about the end of August, when irrigation had been discontinued for some time and the fields dry, a heavy rain fell, and there was an opportunity of estimating what solid matters were removed by the pure water.

100 litres of the water collected as it ran off contained—

Dry residue .....	4.050	grams.	
SiO <sub>2</sub> .....	1.200	„	
Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , FeO ....	0.123	„	
CaO .....	0.049	„	
MgO .....	0.876	„	
Alkalis as chlorides....	1.050	„	
SO <sub>3</sub> .....	0.016	„	
Cl .....	0.350	„	
N <sub>2</sub> O <sub>5</sub> .....	0.190	„	
NH <sub>3</sub> .....	0.046	„	J. F.

**Vegetables used as Food in Japan.** By O. KELLNER (*Landw. Versuchs.-Stat.*, 30, 42—51).—Vegetables form a large part of the people's food in Japan; the varieties in use are many, and the methods of cooking numerous; some are preserved by simple air-drying; others are made into jams, pickled with sugar or acidified. The soja bean is the foundation of an almost universally used sauce, *Schoyu*; of a vegetable cheese, *Miso*; and of a highly albuminous jelly, *Tofu*; a large number of the plants are indigenous, others peculiar to warm climates, and few have hitherto been submitted to chemical examination, the accompanying tables being in many cases the first published analyses. Rice is the largest article of consumption, and of it there are many varieties, all of which are grouped in two divisions: one, the mountain rice grown on dry ground; the other marsh rice, cultivated in irrigated fields, both being botanically the same. Of the marsh rice there are also two principal divisions—ordinary and glutinous rice; the following analyses of dry matter in the three kinds are given:—

	Ordinary.	Glutinous.	Mountain.
Protein matter.....	7.00	5.87	8.75
Fat.....	2.29	3.44	2.58
Cellulose .....	4.58	5.19	1.98
Non-nitrogenous extract..	84.76	83.89	85.53
Ash .....	1.37	1.61	1.18

The figures for fat are larger than in other analyses of rice, but the

	Raphanus sativus.		Brassica rapa rapifera.	Canophollus Konjak.	Colocasia antigonorum.	Aretium Lappa.	Dioscorea japonica.	Batata, yellow flesh.	Batata, white flesh.	Canavalia incurva.	Phaseolus radiatus.	Sorghum.	Millet.	Maize.	Mountain rice.	Marsh rice.	
	1	2															
Water .....	14.20	93.45	93.06	91.76	80.65	73.93	80.74	65.56	64.27	15.28	12.20	12.37	12.04	19.27	12.77	14.20	
<i>Dry substance.</i>																	
Protein matter ....	9.84	13.39	21.00	12.50	10.81	12.34	11.74	5.40	4.12	25.55	20.84	12.34	8.43	15.22	11.27	9.84	
Fat .....	2.66	1.06	0.95	0.98	0.91	0.49	0.84	1.06	3.00	1.76	1.62	6.17	4.40	5.08	2.57	2.66	
Cellulose .....	1.45	13.63	13.47	3.67	3.63	7.47	4.36	3.51	2.74	13.54	6.89	5.32	1.54	2.50	1.62	1.45	
Ash free from C and		11.78															
CO <sub>2</sub> .....	1.02	6.62	9.41	4.42	4.41	3.16	3.60	2.30	1.75	4.24	2.96	5.26	1.26	1.07	1.29	1.02	
Starch .....	77.86	22.45	55.17	75.16	33.70	13.44	22.13	67.77	84.78	44.84	65.38	54.49	51.99	73.72	77.36	77.86	
Cane-sugar, glucose, and non-nitrogen- ous extract .....	10.17	44.70	54.44	—	—	—	—	—	—	—	—	2.47	—	—	—	—	
Total nitrogen ....	1.571	3.471	3.361	3.27	1.729	1.974	1.879	0.865	0.660	3.325	3.325	1.975	1.35	2.435	1.80	1.571	
Nitrogen as albumin	1.441	1.678	1.888	1.58	1.150	0.460	1.204	—	0.458	3.05	3.055	1.738	1.21	2.103	1.34	1.441	
Nitrogen not as albu- min .....	0.130	—	—	—	—	1.514	—	—	0.202	1.04	0.270	0.237	0.11	0.332	0.46	0.130	
Nitrogen precipitated by phosphotungstic acid .....	0.047	1.793	1.473	0.42	0.579	1.007	0.675	—	—	0.81	—	—	—	—	—	0.047	

*Ash Analysis per Cent.*

	Marsh rice.	Mountain rice.	Maize.	Millet.	Sorghum.	Phaseolus radiatus.	Canavalia incurva.	Batata, white flesh.	Batata, yellow flesh.	Dioscorea japonica.	Arecium Lappa.	Colocasia antiquorum.	Conophyllus Konjak.	Brassica rapa rapifera.	Raphanus sativus.	
															1	2
K <sub>2</sub> O.....	22.94	21.73	32.64	20.57	21.44	45.14	35.99	53.27	50.97	57.05	41.61	66.14	54.52	39.06	34.06	46.43
Na <sub>2</sub> O.....	4.94	1.59	1.74	3.34	4.89	2.61	1.85	1.17	4.18	1.28	1.75	0.33	7.22	14.43	12.26	2.40
CaO.....	3.24	2.12	2.21	2.36	2.61	3.49	8.29	12.78	9.66	6.42	10.16	4.16	12.48	11.42	13.27	9.44
MgO.....	10.54	6.61	10.45	14.12	14.48	9.98	7.66	9.23	6.71	9.07	19.01	6.83	5.28	4.65	5.68	4.66
Fe <sub>2</sub> O <sub>3</sub> .....	1.03	1.66	1.28	0.44	1.80	1.09	0.78	0.68	1.29	2.40	2.42	1.18	0.87	1.69	1.30	0.59
P <sub>2</sub> O <sub>5</sub> .....	51.37	51.99	44.13	39.59	49.72	33.05	36.93	8.48	9.28	9.79	8.43	9.11	6.68	6.19	7.27	10.13
SO <sub>3</sub> .....	1.85	2.08	3.48	3.32	2.49	0.91	5.17	4.84	4.28	7.89	6.65	4.55	4.80	13.63	15.07	13.09
SiO <sub>2</sub> .....	3.14	9.63	1.97	11.59	0.22	0.55	0.63	0.64	0.67	1.14	0.63	4.79	0.19	1.97	2.46	2.57
Cl.....	1.05	4.49	1.75	3.73	1.35	2.36	2.15	11.89	12.40	7.99	10.69	3.14	5.70	5.50	6.62	11.94
Deduct O for Cl																
	100.10	101.90	99.65	99.07	99.00	99.18	99.45	102.98	100.00	102.03	101.35	100.23	97.91	98.54	97.99	101.25
	0.24	1.01	0.39	0.84	0.30	0.53	0.49	2.70	2.79	1.80	2.41	0.70	1.49	1.01	1.49	2.69
	99.86	100.89	99.26	98.23	98.70	99.85	98.96	100.28	97.21	100.23	98.94	99.53	96.42	97.53	96.50	98.56



difference is accounted for by the author's samples being undressed grain, whereas the samples examined by other investigators have been of the dressed and well cleaned commercial article. *Panicum italicum*, a species of millet, is, after rice, the principal food of the poorer classes. *Sorghum saccharatum* is an introduction from America. *Phaseolus radiatus* is a bean largely cultivated and highly esteemed; it differs but little from the European variety, *Phaseolus vulgaris*.

*Canavalia incurva*, another sort of bean, is a climber not much cultivated; the pods are about 20 cm. long, bearing 6—8 rose-coloured seeds, weighing on an average 2.5 grams each; they have, when ripe, a disagreeable smell, and are generally eaten unripe. *Solanum melongena*, or egg plant, is largely cultivated, and many varieties of it exist; it is reared from seed, and bears fruit for a long time. The specimen of fruit examined weighed 64 grams; its value as food about equals that of the pumpkin or gourd. Young shoots of the *Bambusa puerula*, and three other varieties of bamboo, are very much in favour. As soon as they appear above the earth in spring, they are dug out and eaten, dressed as asparagus. Different kinds of the sweet potato (*Batatas edulis*) are largely cultivated, and are great favourites; their long succulent stems interlace and cover the soil, keeping it moist. Their deficiency in nitrogen and the small amount of ash compared with other root vegetables, is remarkable.

*Dioscorea japonica* is of limited cultivation, and used by the wealthier classes. *Arctium Lappa*, the seeds of one variety, *Umedda Gobo*, reach an extraordinary size, a length of 1 meter, and circumference of about 30 cm. *Colocasia antiquorum*, the sweet Japanese potato, is extensively cultivated; like the common potato, it is grown from the sliced tubers. *Conophollus Konjak* is a somewhat similar plant; the root is rich in starch; it is used in the preparation of a gelatinous sort of food called konyaku, peeled, dried, and rubbed to powder; milk of lime, or the soluble salts from wood-ash is added to it, and stirred up to a stiff paste; it dries to a clammy mass. *Brassica rapa rapifera*, a turnip, is a favourite food. *Raphanus sativus* is a kind of radish which grows to an enormous size, specimens weighing  $2\frac{1}{2}$ —3 kilos. are not uncommon, and one sort is much esteemed for its sweet taste; the radish is one of the most esteemed vegetable foods of Japan.

J. F.

**Contribution to the Chemical Study of Soils.** By DUGAST (*Ann. Agronomiques*, 9, 470—478).—The author has made very full analyses of three soils, A, B, and C; the first of which always yields better crops than the second, but also always smaller than the third (C). The three soils are from the district of Marché Neuf (Loir Inférieure).

A is a stony soil formed by disintegration of, and resting on, a conglomerate consisting of siliceous fragments of Pliocene age, bound together by a ferruginous cement.

B is a similar soil, but the layer of half-disintegrated subsoil is thicker. B is more stony than A, and contains a notable proportion of organic matter.

C is a stiff clay soil, difficult to work dry or wet, and resting on a subsoil of impermeable clay at a depth of half a metre. The soils

are cultivated in an irregular rotation, comprising a cereal crop followed by two years of pasture or forage crops, and these by two or three years of culture comprising cabbage, beet, buckwheat, rye, potatoes, or maize. The mean produce of wheat is 16—17 hectolitres per hectare.

The samples of soil were taken according to the instructions in Grandean's *Traité d'Analyse des Matières Agricoles*; the surface samples to a depth of 0·2 metre, and the subsoil samples to a second depth of 0·2 metre.

*Mechanical Analysis and Physico-chemical Analysis of the Fine Earth.*—The method devised by Schlösing, and described by Grandean was exactly followed. According to this plan, instead of submitting the crude fine earth to elutriation, the carbonate of lime is first removed by dilute acid, the true clay next washed out by a modified process of levigation; then the humus is removed from the sand by ammonia, and the purified sand is finally separated by elutriation in the ordinary manner into "coarse sand" and "fine sand:"—

	A.	B.	C.
Weight of a litre of crude soil.....	1·212	0·865	1·158 kilos.
Moisture given off at 120° .....	5·820	6·230	6·680 p.c.

*Mechanical Analysis of the Soil dried at 100°.*

	A.	B.	C.	Subsoil A.
Fine earth .....	76·03	71·40	88·65	54·70
Gravelly sand (on sieve 1 mm. mesh) ..	16·01	16·20	1·05	} 45·30
Gravel (on sieve 3 mm. mesh) .....	2·60	1·52	6·45	
Stones (on sieve 5 mm. mesh) .....	5·36	10·88	3·95	
	100·00	100·00	100·00	100·00

*Physico-chemical Analysis of Fine Earth dried at 100°.*

	A.	B.	C.
Humus .....	3·85	6·18	3·25
Sand .....	90·45	87·62	87·71
True clay .....	4·45	4·40	6·75
Carbonate of lime .....	0·41	0·29	0·21
Loss (mattersoluble in acidulated water)	0·84	1·51	1·88
	100·00	100·00	100·00
*Sand obtained by simple levigation ..	42·00	37·00	30·00

\* The difference between these figures and those given above for sand, represents the so-called clay obtained by the ordinary process of elutriation.—J. M. H. M.

*Nitrogen per Cent. of Fine Earth dried at 100°.*

	A.	B.	C.
Organic nitrogen .....	0·1256	0·1739	0·1249
Nitric nitrogen .....	0·0036	0·0027	0·0013
Ammoniacal nitrogen .....	0·0028	0·0004	0·0018
Total nitrogen .....	0·1320	0·1770	0·1290

*Substances Dissolved by Nitric Acid.*

	A.	B.	C.
Phosphoric acid ( $P_2O_5$ ) .....	0·105	0·066	0·087
Lime .....	0·263	0·191	0·216
Magnesia .....	0·075	0·058	0·101
Ferric oxide .....	1·905	1·945	1·823
Sulphuric acid ( $SO_3$ ) .....	0·028	0·026	—
Chlorine .....	0·007	0·004	0·002
Oxide of manganese .....	0·017	0·025	0·009
Potash ( $K_2O$ ) .....	0·126	0·121	0·059
Soda ( $Na_2O$ ) .....	0·018	0·023	0·007
Silica .....	0·045	0·058	0·036
Alumina .....	1·126	1·113	1·723
	3·719	3·630	4·070
Organic matter, sand, and insoluble silicates .....	96·281	96·370	95·930
	100·000	100·000	100·000

The portion insoluble in nitric acid was also analysed, and the results, combined with those just cited, give the following as the absolute composition of the dry fine earth:—

	A.	B.	C.	Subsoil A.
Phosphoric acid .....	0·266	0·113	0·147	0·193
Lime .....	0·576	0·482	0·582	0·630
Alumina .....	7·786	7·217	8·115	6·081
Ferric oxide .....				3·123
Potash .....	0·266	0·278	0·610	0·632
Soda .....	0·057	0·103	0·292	0·275
Silica .....	86·370	84·420	86·330	84·273
Magnesia .....	0·233	0·185	0·388	0·473
Organic matter and unestimated .....	4·446	7·202	3·536	4·320
	100·000	100·000	100·000	100·000

*Proportion and Composition of the "Black Matter."*—The humus here referred to is obtained by heating the fine earth with acidulated water to remove the lime, then washing and exhausting the residue with solution of ammonia:—

	A.	B.	C.
Black matter .....	0·910	2·250	1·138
Phosphoric acid combined with black matter.....	0·036	0·038	0·038

*Composition of Black Matter.*

	A.	B.	C.
Total ash .....	15·50	22·50	37·950
Phosphoric acid.. ..	3·95	1·68	3·307
Alumina and ferric oxide.....	—	—	17·300
Lime .....	—	—	0·663
Magnesia .....	—	—	0·105
Potash.....	—	—	0·147
Soda .....	—	—	0·026

*Phosphoric acid per cent. of fine dry earth soluble in the following reagents:—*

	A.	B.	C.
Aqua regia .....	0·108	0·072	—
Oxalate of ammonia .....	0·056	0·048	—
Citrate of „ .....	0·042	0·034	0·012
Acetic acid .....	0·018	0·013	—
Water saturated with CO <sub>2</sub> .....	0·015	0·013	—
Distilled water .....	0·012	0·011	—

Phosphoric acid in gravelly sand ..... 0·0099 per cent.

Potash in gravelly sand ..... 0·0400 „

Potash, lime, and magnesia are deficient in all three soils, and phosphoric acid in B and C; the deficiency in phosphoric acid rendering B less fertile, notwithstanding its good supply of nitrogen. Soil C, naturally the most fertile of the three, has been partially exhausted by successive cereal crops.

J. M. H. M.

**Examination of certain Soils in Japan.** By O. KELLNER and H. IMAI (*Landw. Versuchs.-Stat.*, 30, 1—17).—Many visitors to Japan praise the richness of the vegetation and the fertility of the soil. The author, agricultural chemist at the College of Tokio, says that from a

study of the weeds and wild plants natural to the country, it is evident that the soil is not rich, but that the luxuriance of certain crops at their season is caused principally by the method of manuring, which consists in applying the manure at frequent intervals during the growth of the crops, and in the immediate neighbourhood of the roots; the furrows in which seeds are sown and the holes into which plants are set, are all carefully prepared with manure. The Japanese also have a strong objection to break up new ground unless they have the necessary quantity of manure at hand, and have a custom of planting exhausted fields with nut trees so as to prepare the soil for being again broken up.

Trustworthy examinations of the ordinary arable soil, and comparison with the land under rice plantations, had not yet been made when the author undertook them at the experimental farm of the College, the soil of which was of volcanic origin, containing much iron and soluble silicates; a portion of the farm was laid out as a rice field. The chemical analysis is given in Table I:—

TABLE I.

	Dry field.		Rice field.	
	Soil.	Subsoil.	Soil.	Subsoil.
Hygroscopic water..	15.49	18.69	14.30	12.84
Loss on ignition....	20.01	14.90	22.30	18.79
Humus .....	7.90	7.17	9.96	8.86
Nitrogen .....	0.80	0.60	0.489	0.799
Combined water....	11.31	7.13	11.85	9.13

The soils of both fields, dried at 100° and extracted with cold hydrochloric acid of sp. gr. 1.15, gave the results shown in the following table:—

	Earth of dry field.		Earth of rice field.	
	Soil.	Subsoil.	Soil.	Subsoil.
SiO <sub>2</sub> .....	0.31	0.29	0.82	0.79
Al <sub>2</sub> O <sub>3</sub> .....	15.93	19.73	15.50	14.15
Fe <sub>2</sub> O <sub>3</sub> .....	11.73	11.36	7.00	7.49
CaO .....	0.60	0.66	0.75	0.70
MgO .....	1.41	1.44	0.45	0.55
K <sub>2</sub> O .....	0.29	0.18	0.10	0.17
Na <sub>2</sub> O .....	0.17	0.13	0.14	0.01
P <sub>2</sub> O <sub>5</sub> .....	0.19	0.18	0.37	0.35
SO <sub>3</sub> .....	0.11	0.12	0.18	—
	30.74	34.09	25.31	24.21
Insol. residue ....	48.30	49.48	50.00	51.16
Humus and combined water....	23.67	18.33	26.02	25.83
	102.71	101.90	101.33	101.20

A circumstance which greatly modifies the nature of the surface soil in Japan, is the continuance of long droughts and high winds, the fine sandy soils become very fine dust, and is blown in great clouds over the face of the country, collecting behind hedges and walls after the manner of snow-drifts; in some places it is heaped up in large quantities, the rice fields being less dry do not suffer, but retain some of the dust from arable soils; the farmers prize this highly; but any analysis of the surface soil under such conditions cannot be of permanent value. J. F.

**Determinations of Nitrogen in the Soils of Experimental Fields at Rothamsted, and Bearing of the Results on the Question of the Sources of the Nitrogen of our Crops.\*** By SIR J. B. LAWES and J. H. GILBERT (*Ann. Agronomiques*, 9, 393—418, 451—465).—Included in the scheme of the experimental fields at Rothamsted there are certain plots on which wheat, barley, roots, beans, clover, and ordinary rotation crops have each been grown, year after year, either without any manure or with a purely mineral (non-nitrogenous) manure for periods, in some instances, of over 40 years.

Determinations of the nitrogen contained in these crops have been regularly made, and at certain intervals the soil of each plot has been sampled, as well as the soils of adjacent plots receiving various nitrogenous manures, and the nitrogen per acre contained in the fine mould of these soils to a certain depth has been carefully estimated. The results of these determinations are set forth in the present paper and discussed in connection with the question, whether our farm crops derive any considerable proportion of their nitrogen from other sources than the soil and manure. The annexed table (p. 683) shows the yield of nitrogen per acre per annum in the various crops grown without nitrogenous manure.

*Root Crops.*—The results with mineral manure only are given, as without any manure the produce becomes almost *nil* after a few years. The average yield of nitrogen is very much higher in the first few years with root crops than with either wheat or barley, and the subsequent decline is much more rapid.

*Leguminous crops*, such as beans and clover, which are said by some to rely almost exclusively on atmospheric sources for their nitrogen, nevertheless fall off in yield in a most striking manner when not supplied with nitrogenous manures, even although abundance of mineral manure is provided. The clover crop succeeded only in 6 years out of the 22. The nitrogen yielded by these crops is very much greater than in the case of the cereals or roots, but the decline after the first few years is extremely marked.

*Rotation of Crops.*—As only the average yield of the whole 28 years is given, a decline in nitrogen cannot be inferred from these figures. The effect of rotation is to raise very considerably the yield of nitrogen over that given by cereal crops grown successively. A dressing of superphosphate increases the nitrogen in the turnip crop, reduces

\* This Abstract is from the original paper read before the American Association at Montreal, August, 1882. (London, Harrison and Sons, 1883.)—J. M. H. M.

it in the succeeding barley, greatly increases it in the clover, and slightly in the succeeding wheat. In an adjoining plot where fallow was substituted for clover, the nitrogen yielded by the rotation was very much less.

TABLE I.

TABLE I.					Average nitrogen per acre per annum.				
Wheat .....	{	Unmanured .....	8 years, 1844—51	25.2 lbs.					
			12 " 1852—63	22.6	"				
			12 " 1864—75	15.9	"				
			24 " 1852—75	19.3	"				
			32 " 1814—75	20.7	"				
			12 " 1852—63	27.0	"				
			12 " 1864—75	17.2	"				
			24 " 1852—75	22.1	"				
Barley .....	{	Complex mineral manure ....	12 " 1852—63	22.0	"				
			12 " 1864—75	14.6	"				
			24 " 1852—75	18.3	"				
			12 " 1852—63	26.0	"				
			12 " 1864—75	18.8	"				
			24 " 1852—75	22.4	"				
			Root crops ..	{	Unmanured .....	Turnips .. 8	1845—52	42.0	"
						(Barley) .. 3	1853—55	(24.3)	"
Turnips .. 15	1856—70*	18.5				"			
Sugar-beet. 5	1871—75	13.1				"			
Mangel.... 5	1876—80	15.5				"			
Total .... 36	1845—80	25.2				"			
Beans .....	{	Complex mineral manure ....				12 " 1847—58	48.1	"	
						12 " 1859—70†	14.6	"	
			24 " 1847—70	31.3	"				
			12 " 1847—58	61.5	"				
			12 " 1859—70†	29.5	"				
			24 " 1847—70	45.5	"				
			Clover .....	{	Unmanured .....	22 " 1849—70‡	30.5	"	
						22 " 1849—70‡	39.8	"	
Clover .....	{	Complex mineral manure ....	1 " 1873 ....	37.3	"				
Barley .....			1 " 1873 ....	151.3	"				
Barley .....	{	Unmanured..	After barley.. 1	1874 ....	39.1	"			
			After clover .. 1	1874 ....	69.4	"			
Rotation courses	{	1. Turnips..... 2. Barley..... 3. Clover or beans .. 4. Wheat .....	Unmanured	28 " 1847—75	36.8	"			
				Superphos- phate ..	28 " 1847—75	45.1	"		

*Mixed Herbage of Grass Land.*—The yield of nitrogen and the botanical composition of the crops from the plots which received no nitrogenous manure, are given in Table II (p. 684).

In interpreting this table, it should be borne in mind that gramineous crops contain much less nitrogen than leguminous crops; nevertheless, nitrogenous manures have a striking effect in increasing their growth. Leguminous crops, although containing much nitrogen, do not respond to nitrogenous manures, but are largely increased by mineral manures, especially potash. The first three plots show a

\* Thirteen years crop, two years failed.

† Nine years beans, one year wheat, two years fallow.

‡ Six years clover, one year wheat, three years barley, twelve years fallow.

marked falling off in nitrogen yielded; the fourth, in which the Leguminosæ were greatly encouraged by the application of potash, shows, on the contrary, a slight tendency to increased yield. It is noteworthy that mineral manures applied to mixed herbage increase the yield of Gramineæ much more than when applied to the Gramineæ grown separately.

TABLE II.

	Average produce per acre per annum, 20 years, 1856—1875, according to mean per cent. at six periods, 1862, '67, '71, '72, '74, '75.			Average nitrogen per acre per annum.		
				10 years, 1856—65.	10 years, 1866—75.	20 years, 1856—75.
	Grami- neæ.	Legumi- nosæ.	Other orders.	lbs.	lbs.	lbs.
Unmanured . . . . .	1635 lbs.	219 lbs.	529 lbs.	35·1	30·9	33·0
Superphosphate* . . .	1671 „	149 „	673 „	35·7	31·5	33·6
Complex mineral manure† . . . . .	2442 „	296 „	639 „	54·4	33·1	46·3
Complex mineral manure‡ . . . . .	2579 „	806 „	573 „	55·2	56·0	55·6

*Melilotus Leucantha* (*Bokhara Clover*).—This plant has been grown since 1878 on a plot which had been devoted to unsuccessful attempts to grow red clover consecutively from 1849. For 30 years this plot had received no nitrogenous manure, yet it has yielded crops of *Melilotus* averaging 70 lbs. nitrogen per acre per annum 1878–81, whilst the crop of the fifth year, 1882, is still more luxuriant, and is estimated to contain 150 lbs. nitrogen.

From the foregoing it will be seen that in all the experiments on ordinary arable land, with or without mineral manure, *the decline in the annual yield of nitrogen, none being supplied by manure, was very great.* Bokhara clover is, so far, an exception.

The authors go on to consider the amount of combined nitrogen annually supplied to the soil by rain, and after citing all the published determinations of nitric and ammoniacal nitrogen in the rainfall over given periods, they conclude that not more than 5 lbs. of nitrogen per acre per annum is supplied to the soil of Rothamsted from this source. Passing in review the well-known researches of Boussingault, and of Lawes, Gilbert, and Pugh, on the one side, and of Ville on the other, extending from 1837 to 1858, they reaffirm their conviction that the evidence is strongly against the supposition that either the Gramineæ or the Leguminosæ assimilate the free nitrogen of the atmosphere. They next consider the evidence furnished by analysis

\* Mean of four separations only, 1862, '67, '72, '75.

† Including potash, 6 years, 1856–61; without potash, 14 years, 1862–75.

‡ Including potash, 20 years, 1856–1875.



of the soils of the Rothamsted plots as to the source of the greater part of the nitrogen of crops.

*Nitrogen in the Soils of Experimental Wheat Plots.*—Passing over isolated samples of soil taken in the early years of the series, and in 1856, as not being sufficiently numerous or uniform, there remain for comparison the samplings of 1865 and 1881. In 1865, eleven plots were sampled, eight samples from each plot being taken, each sample 12 × 12 inches area with a total depth of 27 inches, divided into three portions of 9 inches each. In 1881, twenty plots were sampled; the samples (six to each plot) were 6 × 6 inches in area, and again taken to a depth of 27 inches in three successive instalments of 9 inches. The various samples of surface soil (first 9 inches) from each plot were mixed, a portion of each, however, being kept to furnish check analyses. The mixed samples were broken up, dried at 130° F. to arrest nitrification, the stones removed by successive sieves of 1-inch,  $\frac{1}{2}$ -inch, and  $\frac{1}{4}$ -inch mesh, and the remaining *fine mould* powdered and sifted for analysis, the result being calculated on the *fine mould dried at 100° C.* The two series of subsoil samples (second and third 9 inches) were treated in a similar manner, but the results are given for the surface soils only. The calculated quantity of dry mould per acre (first 9 inches) was in 1865 (mean of 80 samples) 2,299,038 lbs., and in 1881 (mean of 114 samples) 2,552,202 lbs., showing that the state of consolidation of the soil was different at the two periods. The normal quantity of fine mould per acre (first 9 inches) is assumed to be 2,300,000 lbs., and the results obtained in 1881 are corrected by supposing the samples to contain one-tenth of their weight of subsoil (second 9 inches), and proportionately raising the percentage of nitrogen in the remaining nine-tenths. The actual and corrected results are in Table III (p. 686).

During the 16 years from 1865 to 1881, therefore, the three plots (3, 5a, 16a) receiving no nitrogen as manure have suffered a very striking decrease in the nitrogen contained in their surface soils; whilst the other plots, receiving nitrogenous manure, show in some cases a slight loss, in others, a gain. The excess of nitrogen in these latter plots over that in Plot 5a (complete mineral manure without N) varies considerably, as shown in the table; it has no relation to the quantity of nitrogen supplied in the manure, but, as shown by the authors in a supplementary table, it is directly related to the average crop yielded by each plot. In other words, loss of manurial nitrogen is not prevented by any retentive property of the soil, but by its conversion into crop residue—stubble and roots—which varies with the amount of crop. The authors estimate that in the 30 years, 1852–81, the unmanured plot yielded an average of 18·6 lbs. nitrogen in the crop, and lost 10·3 lbs. in the drainage—a total loss of 28·9 lbs. per annum over that period. In like manner, Plot 5 yielded an average of 20·3 lbs. N in the crop, and 12 lbs. in the drainage, in all 32·3 lbs. per acre per annum. About 30 lbs. N per acre per annum therefore has been contributed from some source to crop and drainage together. Analysis shows a loss of about two-thirds of this amount annually to a depth of 27 inches. There remains, therefore, about 10 lbs. to be contributed by seed, by rain, and condensation from the atmosphere,

TABLE III.

*Experimental Wheat Plots. Nitrogen per cent. in the Dry Mould and per Acre (1st 9 inches).*

Plots.	Manures, per acre, per annum (as in 1851-52, and since)	Nitrogen.									
		Per cent. in dry mould.			Per acre, 2,300,000 lbs. of dry mould.						
		1865.	1881.		1865.	1881.	1881 + or - 1865.	+ or - plot 5a.			
		Actual.	Actual.	Corrected.	1865.	1881.	1881 + or - 1865.	1865.	1881.	1881 + or - 1865.	
		Per cent.	Per cent.	Per cent.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	
3	Unmanured (1843-44 and since) ..	0.1090	0.1009	0.1045	2507	2404	-103	—	—	—	
5a	Mixed mineral manure .....	0.1119	0.0981	0.1012	2574	2328	-246	—	—	—	
7a	Mixed mineral manure and NH <sub>3</sub> salts = 86 lbs. N .....	0.1230	0.1207	0.1264	2829	2908	+ 79	+ 255	+ 580	+ 325	
9a	Mixed mineral manure and NaNO <sub>3</sub> = 86 lbs. N .....	0.1232	0.1200	0.1253	2834	2883	+ 49	+ 260	+ 555	+ 295	
10a	NH <sub>3</sub> salts = 86 lbs. N (1845 and since) .....	0.1108	0.1034	0.1074	2548	2471	- 77	- 26	+ 143	+ 169	
11a	NH <sub>3</sub> salts = 86 lbs. N. and superphosphate .....	0.1171	0.1121	0.1164	2693	2676	- 17	+ 119	+ 348	+ 229	
12a	NH <sub>3</sub> salts = 86 lbs. N, superphosphate, and sodium sulphate .....	0.1208	0.1155	0.1202	2778	2765	- 13	+ 204	+ 437	+ 233	
13a	NH <sub>3</sub> salts = 86 lbs. N, superphosphate, and potassium sulphate ..	0.1206	0.1191	0.1245	2774	2803	+ 89	+ 200	+ 535	+ 335	
14a	NH <sub>3</sub> salts = 86 lbs. N, superphosphate, and magnesium sulphate ..	0.1197	0.1163	0.1215	2754	2793	+ 41	+ 179	+ 466	+ 287	
16a	NH <sub>3</sub> salts = 172 lbs. N, and mixed mineral manure* .....	0.1264	0.1066	0.1112	2907	2557	- 350	+ 333	+ 229	- 104	

\* 13 years to 1864 ; unmanured since.

and by all the other supplies of combined nitrogen which have been supposed to be available. Of this about 2 lbs. will be due to seed, and supposing only 5 lbs. annually to be supplied by rain and minor aqueous deposits, there is but little left to be provided by all the other sources assumed.

*Nitrogen in Soil of Barley Plots.*—In 1868, four samples, 6 × 6 inches by 9 inches deep, were taken from each of four plots; only one of these plots had received no nitrogenous manure. In 1882, twenty-six plots were sampled to a total depth of three times 9 inches, four samples, 6 × 6 inches area, being taken from each plot. The plot which received mixed mineral (non-nitrogenous) manure alone contained in 1868, 0·1202 per cent. N in the first 9 inches of dry mould; in 1882, 0·1124 per cent. N.

*Nitrogen in the Soil of Root Plots.*—These plots have carried roots (turnips, swedes, sugar-beet, or mangel) for 40 successive years (1843–1882), with the exception of 3 years, in which barley was sown. The soils were sampled only in 1870, so that no comparison at different dates is yet possible. Some of the percentages of N found in 1870 are—

Plot 3. Unmanured .....	0·0852	per cent. N (in 1st 9 ins.).
„ 4. Mixed mineral manure....	0·0934	„ „ „
„ 5. Superphosphate only ....	0·0888	„ „ „
„ 6. Superphosphate and potash	0·0867	„ „ „
Mean of Plots 4, 5, and 6....	0·0896	„ „ „

These plots, after receiving no nitrogenous manure for 27 years, show a smaller percentage of nitrogen in the surface soil than has been found in any of the other experimental fields.

*Nitrogen in the Soil of Bean Plots.*—The determinations are not given, but are stated to lead to the conclusion that there has been a gradual decrease of nitrogen in the surface soil.

*Nitrogen in the Soil of Clover Plots.*—The want of success attending all attempts to grow clover continuously on the same plot, renders only a few special comparisons possible. The red clover plot, which yielded only six clover crops from 1849–1870, and very few afterwards, was sampled in 1881 in five places to a depth of 9 inches for comparison with an adjoining wheat plot 30 years under alternate wheat and fallow. Neither of these plots had received any nitrogenous manure for 30 years.

*Nitrogen per Cent. in 1st 9 inches of Dry Mould (1881).*

	Clover land.	Wheat and fallow.
Mean of determinations on 5 separate samples..	0·1067	0·0925
Mean on the mixture of the 5 samples.....	0·1055	0·0984
Mean .....	0·1061	0·0955

The N in the surface soil of the clover plot is low, and has probably declined, although it is higher than in the adjacent wheat and fallow plot.

The next results refer to the plot (see Table I) which in 1873 had grown six successive corn crops by artificial manures alone, and was then divided, one-half carrying barley, and the other clover. In 1874 barley was taken on both halves. In 1873 the barley crop contained 37·3 lbs. N, and the clover crop 151·3 lbs. N. In 1874 the barley after barley yielded 39·1 lbs. N, whilst the barley after clover yielded 69·4 lbs. N, so great an improvement had the previous year's clover crop effected, notwithstanding the fact of the large quantity of nitrogen removed in that clover crop. The soil was sampled in October, 1873, with the results given in Table IV:—

TABLE IV.

*Nitrogen per Cent. in 1st 9 inches of Dry Mould (1873).*

	Clover land.	Barley land.
Sample No. 1 (12 × 12 × 9 inches) ..	0·1574	0·1468
„ No. 2 (12 × 12 × 9 „ ..	0·1529	0·1341
„ No. 3 (12 × 12 × 9 „ ..	0·1484	0·1431
„ No. 4 (12 × 12 × 9 „ ..	0·1631	0·1405
Mean on the four separate samples (12 × 12 × 9 inches) .....	0·1554	0·1411
Mean on a mixture of the four samples (12 × 12 × 9 inches) .....	0·1566	0·1387
Mean on a mixture of six samples (6 × 6 × 9 inches) .....	0·1578	0·1450
General mean .....	0·1566	0·1416

These results illustrate forcibly the necessity of taking numerous samples, but the mean of the three sets of determinations leaves no doubt that the surface soil of the clover plot contained a considerably higher percentage of nitrogen than that of the barley plot—and this, too, after all visible vegetable *débris* had been removed as completely as possible. Samples taken in 1877 still showed a higher percentage in the clover plot than in the barley. It is obvious that the surface soil of the clover plot gained nitrogen either from the atmosphere or from the subsoil—and, so far as the determinations of nitrogen in the subsoils go, the indication is that if from below it is at least mainly from a lower depth than 27 inches. The authors observe that it is natural to assume the atmosphere as the source of this nitrogen, but that there is absolutely nothing in favour of this view excepting the fact that an explanation is needed; whilst there is much more evidence in favour of the view that the subsoil has been the source of at least much of it.

*Soils of Melilotus Leucantha and White Clover Plots.*—The soil of the melilotus plot was sampled in 1882, after the fifth large consecutive crop on soil which had repeatedly refused to grow clover, and to which no nitrogenous manure had been applied for 30 years. A sample of soil from the corresponding white clover plot was taken at the same time, in each case to a depth of six times 9 inches, in all

54 inches. The examination of these samples is still incomplete, but the following evidence is forthcoming. The strong roots of the melilotus were found to penetrate to the lowest depth of the samplings, the soil being disintegrated, and having lost approximately 540 tons per acre more water than the corresponding 54 inches of white clover soil, in which there was very little development of root below the first 9 inches. Determinations of nitric acid in the two soils gave the results recorded in Table V :—

TABLE V.

	Per million, dry soil.		Per acre.		
	Melilotus soil.	White clover.	Melilotus soil.	White clover.	Difference.
			lbs.	lbs.	lbs.
First 9 inches. ....	1·28	3·24	3·39	8·59	5·20
Second 9 inches. ....	0·36	1·10	0·97	2·97	2·00
Third 9 inches. ....	0·21	0·66	0·61	1·91	1·30
Fourth 9 inches. ....	0·33	1·03	0·99	3·09	2·10
Fifth 9 inches. ....	0·28	1·46	0·84	4·38	3·54
Sixth 9 inches. ....	0·55	1·77	1·65	5·31	3·66
Total. ....	—	—	8·45	26·25	17·80

There is here direct evidence that the soil is the source of at least some of the excess of nitrogen of the melilotus over that in the white clover.

The authors next adduce determinations of nitrogen as nitric acid in various soils, in order to show the amount available for vegetation. Thus the soil of the unmanured wheat plot contained in October, 1881, 9·7 lbs. per acre nitric N in first 9 inches, 5·2 lbs. in second 9 inches, and 2·8 lbs. in third 9 inches; total, 17·7 lbs. N per acre. The soils of three of the wheat plots which had received nitrogenous manures in the form of ammonium sulphate or sodium nitrate contained 39·9, 38·8, and 54·4 lbs. nitric nitrogen per acre respectively in the first 27 inches. Samples collected from four of the rotation plots in September, 1878, showed in the first 18 inches :—

N as nitric acid after fallow, 36·3 and 48·8 lbs. per acre,

N as nitric acid after beans, 10·6 and 20·5 „ „

the larger quantity being in the plots receiving nitrogenous manure.

Samples taken at the same time to the same depth on the alternate wheat and fallow plots showed :—

N as nitric acid after fallow, 33·7 lbs. per acre.

N as nitric acid after wheat, 2·6 „ „

Samples taken from two other fields after a year's fallow contained in 27 inches depth, 58·8 and 56·5 lbs. N as nitric acid per acre.

These figures indicate a considerable amount of nitrogen available

after fallow, which disappears during the growth of a crop, but it is admitted that they do not show enough nitric nitrogen in the depths examined, to account for the large accumulation of nitrogen in the crop and in the surface soil observed in the case of the experimental clover and barley soils.

*Nitrogen in the Soils of the Experimental Mixed Herbage Plots.*—On referring to the table given above, it will be seen that the plot receiving complete mineral manure yielded 22·6 lbs. N per acre per annum above that yielded by the unmanured plot. Analysis of the soils indicates that the soil of the mineral manured plot has become impoverished in nitrogen to a greater degree than that of the unmanured plot. The results of the first 9 inches of soil are :—

	1870. Per cent.	1876. Per cent.	1878.
Plot 3. Unmanured .....	0·2517	0·2466	—
Plot 7. Mixed mineral manure with potash ..	—	0·2236	—

The quantity of nitrogen lost by Plot 7 over Plot 3 amounts to 506 lbs. per acre over the 20 years of experiment, equal 25·3 lbs. per acre per annum, in this case showing a remarkable correspondence with the excess of nitrogen carried off in Plot 7, viz., 22·6 lbs. per acre per annum. The leguminous plant most encouraged by the mineral manure of Plot 7 was *Lathyrus pratensis*, which threw out a great mass of roots in the surface soil.

*Source of the Nitrogen of Clover grown on Rich Garden Soil.*—Although all attempts to grow red clover continuously on ordinary arable land have been unsuccessful, it has been grown for 29 years in succession on a small plot of rich garden soil. The experiment was commenced in 1854; the soil was sampled in 1857 and 1879. The nitrogen in the first 9 inches is given below :—

1857. Nitrogen per cent. of dry mould 0·5095 = 9528 lbs. per acre.

1879.       "       "       "        $\left\{ \begin{array}{l} 0·3635 \\ 0·3640 \\ 0·3626 \end{array} \right\} = 6796 \text{ " " (mean).}$

In accordance with this large decline of soil nitrogen, there has been a decided falling off in the crops obtained, the produce from the three sowings of the first 14 years, being nearly double of that from the ten sowings which were found necessary to keep up a plant during the next 15 years. Estimating the average yield of nitrogen at 200 lbs. per acre per annum over the 21 years, the nitrogen lost by the surface soil (first 9 inches) is 130 lbs. per acre per annum, or about two-thirds of that carried off by the clover. The authors admit in this case the possibility of a loss by the soil of free nitrogen, and do not include the loss by drainage; on the other hand they point out that some of the nitrogen of the clover was doubtless supplied by the subsoil. They remark that there are very strong grounds for con-

cluding that much, and perhaps the whole, of the nitrogen of the clover was derived from the soil.

Summing up on the whole paper, they submit that there is much more of direct experimental proof of the soil than of the atmosphere as the source of the nitrogen of our crops, both cereal and leguminous. If this be accepted it follows that the fertility of arable soil is to some extent measured by its stored-up nitrogen, and that soil is in fact a "mine" as well as a laboratory.

J. M. H. M.

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## Analytical Chemistry.

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**Determining Left-handed Rotation with the Scheibler-Ventzke-Soleil Polariscopes.** By G. S. EYSTER (*Chem. News*, **49**, 67).—The author suggests the use of a quartz plate of known dextro-rotatory power, with lævorotatory solutions of less rotating power. The difference between the reading with the quartz plate alone and the reading with the quartz plate and solution together is then, obviously, the lævorotatory power of the solution. This is for use with instruments not graduated for left-handed rotations.

D. A. L.

**Litmus, Rosolic Acid, Methyl-orange, Phenacetolin, and Phenolphthaleïn as Indicators.** By R. T. THOMSON (*Chem. News*, **49**, 32—35, 38—41).—In previous communications (Abstr., 1883, 612, 824, and 827) the author has published the results of his investigations on the use of these indicators in the analysis of some potassium, sodium, and ammonium compounds, and of free acids. He has now extended this useful work to the analysis of a few calcium, barium, and magnesium compounds.

*Application of the Indicators to the Determination of Lime as Hydroxide in Presence of a Small Proportion of Carbonate.*—For each experiment in this series, 200 c.c. of lime-water, previously treated in the cold with 0·0265 gram of sodium carbonate, and containing 0·2724 gram of total lime (CaO), 0·2584 as hydroxide, and 0·014 gram as carbonate, were titrated with  $\frac{N}{2}$  hydrochloric acid, a deduction being made for the sodium hydroxide produced by the action of the sodium carbonate. The results obtained are as follows:—

Indicator.	Total CaO found.	CaO as hydrate found.	CaO as carbo- nate found.
	grams.	grams.	grams.
Litmus .....	0·2716—0·2730	—	—
Rosolic acid .....	0·2716—0·2716	—	—
Methyl-orange .....	0·2716—0·2716	—	—
Phenacetolin .....	0·2730—0·2716	0·2562—0·2576	0·0154—0·0154
Phenolphthaleïn .....	0·2716—0·2716	0·2590—0·2576	0·0140—0·0154



With *litmus* or *rosolic acid*, titration is conducted in the cold until change of colour takes place; the solution is then boiled, and the addition of standard acid continued until a permanent change of colour is effected. *Methyl-orange* is not altered by carbonic anhydride, therefore boiling is not necessary when it is used as indicator. *Phenacetolin* (compare Lunge, Abstr., 1883, 828) may be used for the determination of lime, both as hydroxide and carbonate, the changes being the same as already described (*loc. cit.*, 683), viz., rose for hydroxide, subsequent change to yellow for carbonate. Liberated carbonic anhydride must be boiled off. When using this indicator for the determination of lime as hydroxide, the final change of colour is not very distinct, owing to the interference of carbonic anhydride. *Phenolphthaleïn* behaves with lime as with soda (*loc. cit.*), the whole of the lime as hydroxide, and only half that as carbonate being estimated, calcium hydrogen carbonate being neutral. The total lime can be determined by adding excess of standard acid and titrating back. Experiments prove that light flocculent calcium carbonate, freshly precipitated from a cold solution, gives an alkaline reaction with phenolphthaleïn, whilst after boiling, when it is dense and granular, it gives no reaction with this indicator, and therefore calcium hydroxide can safely be determined in the presence of calcium carbonate by simply adding standard hydrochloric acid to a boiling solution, until the red colour of the phenolphthaleïn is gone.

Comparative experiments in which lime and carbonic anhydride were determined in a sample of slaked lime by the ordinary gravimetric methods, and by titration, using phenolphthaleïn as indicator, prove that the results obtained in the two cases are practically the same. *Determination of Lime as Carbonate*: in addition to the above remarks, it may be noted that *litmus*, *rosolic acid*, *phenacetolin* and *methyl-orange* can be used with advantage in this determination, especially for the light flocculent carbonate, the first three are not so delicate with the dense form. *Phenolphthaleïn* is already fully discussed. *Determination of Barium Hydroxide and Carbonate*: the results obtained with lime are equally true of barium. Barium carbonate even when precipitated in the cold is neutral to phenolphthaleïn.

*Determination of Magnesium Hydroxide and Carbonate*.—Total magnesia can be determined by dissolving in excess of standard acid, expelling carbonic acid and titrating back; any indicator being used. Magnesia as hydrogen carbonate can be determined directly with standard acid either in the cold with methyl-orange or in the boiling solution with any of the other indicators. Phenacetolin and phenolphthaleïn cannot be employed successfully for the determination of magnesium hydroxide in the presence of carbonate. The author alludes to Hehner's method for the determination of the hardness of water (*Analyst*, 8, 77), in which the temporary hardness is best estimated by titrating a hot solution, using phenacetolin, whilst for the permanent hardness the calcium and magnesium salts are converted into carbonates by boiling with a measured excess of standard sodium carbonate; the precipitate is filtered off, and the excess of sodium carbonate titrated with standard acid. It is necessary in such determinations to take into account any sodium carbonate present in the water.

*Calcium, Barium, and Magnesium Chloride, Nitrate, and Sulphate*, are neutral to all the indicators with the exception of methyl-orange, which requires more standard acid to produce the final full change of colour when these salts are present than when they are absent. Barium and calcium carbonate being neutral to phenolphthaleïn (see above), the amount of calcium may be determined in any neutral salt or barium in its chloride by titrating with sodium carbonate in the following manner. Add phenolphthaleïn to the solution to be examined; if acid neutralise with sodium hydroxide, then add standard sodium carbonate until a permanent red is developed. These determinations cannot be made in the presence of magnesium.

*Calcium and Magnesium Sulphites*.—For each experiment, 0.525 gram of normal calcium sulphite =  $\text{CaO } 0.242$  was employed. Magnesium sulphite acts in the same way. The results are—

Indicator.	c.c. $\frac{N}{2}$ hydrochloric acid consumed.	Grams $\text{CaO}$ found.
Litmus .....	8.5	0.1190
Rosolic acid { cold .....	—	trace
{ boiling.....	0.4—0.5	0.0056—0.0070
Methyl-orange.....	8.7—8.75	0.1218—0.1225
Phenacetolin .....	8.5	0.1190
Phenolphthaleïn { cold....	—	trace
{ boiling.	—	—

The *litmus* and *phenacetolin* reactions are both unsatisfactory, and as is evident from the appended table, calcium (magnesium) hydrogen sulphite is neutral to them as well as to *methyl-orange* which, however, gives a delicate end-reaction. The normal salt is neutral to *rosolic acid* and *phenolphthaleïn*, to the former only in the cold, to the latter both when cold and boiling. Upon this last fact is founded a method for the estimation of sulphurous anhydride, which gives good results when compared with the iodine method. The method of procedure is as follows: methyl-orange is added to the sample under examination, which is neutralised either with hydrochloric acid or caustic soda, phenolphthaleïn or rosolic acid is now added, and normal or half-normal sodium hydroxide run in until the characteristic colour appears. The number of c.c. used during the second stage multiplied by 0.064 equals grams of sulphurous anhydride present. Phosphoric acid and carbonic anhydride interfere with this reaction.

*Calcium, Magnesium, Potassium, and Ammonium Borates* behave like sodium borate already described (Abstr., 1883, 825), and therefore can only be titrated with methyl-orange as indicator.

*Calcium Phosphates*.—Tricalcium phosphate is neutral to all indicators, monocalcium phosphate is neutral to *methyl-orange*, and acid to the other four. Attempts were made to determine the amount of monocalcium phosphate in presence of calcium chloride by the combined use of methyl-orange and phenolphthaleïn, and titration with  $\frac{N}{2}$  soda, the results were always too high owing to formation of a basic phosphate. With regard to Mollenda's method for determining

phosphoric acid in superphosphate (*Chem. News*, **47**, 231), the author finds that even when indicators are used, only approximate results are obtained.

*Phenol* is neutral to litmus, rosolic acid, methyl-orange, and phenacetolin, and does not destroy the colour. Titration with *phenolphthalein*, the reaction is not distinct. In an experiment with sodium sulphide prepared from hydrogen sulphide and caustic soda, on adding acid in excess, the colour of methyl-violet was destroyed.

The paper concludes with a tabulated arrangement of all the results obtained both on the present occasion and on the previous occasions already referred to. The following is a summary of the table.

With K, Na,  $\text{NH}_4$ , Ca, and Ba *hydroxides*, all five indicators give good results and delicate end-reactions, with the exception of phenolphthalein with ammonia.

With K, Na, Ca, Ba, Mg *carbonates*, K, Na, Ca *hydrogen carbonates*, K, Na *sulphides*, and Mg *oxide*, methyl-orange alone is good in the cold, and all the others are good in boiling solutions, except phenolphthalein with Ba and Ca *carbonates* and Ca *hydrogen carbonate*. With  $\text{NH}_4$  *carbonate* and *sulphide*, methyl-orange alone is good; all the others except phenolphthalein may be used if excess of acid is added and subsequently titrated back. With K, Na, Ca, Mg, and  $\text{NH}_4$  *sulphites*, K, Na,  $\text{NH}_4$  *hydrogen phosphates*, methyl-orange indicates for 50 per cent. of base present, and gives delicate end-reactions. The other indicators are uncertain or indicate for smaller quantities only. K, Na, Ca *dihydrogen phosphates* are neutral to methyl-orange, and acid to all the others. For K and Na *silicates*, litmus and methyl-orange are best, the others, phenolphthalein excepted, are good. For Na, K,  $\text{NH}_4$ , Ca, and Mg *borates*, methyl-orange alone is efficient. In the presence of freshly precipitated *alumina*, phenacetolin and phenolphthalein only are useful for estimation of alkalis. All are good for titration of acids, and give delicate end-reactions with HCl,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , whilst litmus, rosolic acid, and phenolphthalein only are good for *oxalic acid*, and phenolphthalein alone for  $\text{AcHO}$ ,  $\text{Ti}(\text{HO})_2$ , and  $\text{Ci}(\text{HO})_3$ . Phenolphthalein can be employed as indicator in the titration of several fatty and resin acids and natural fats with standard alcoholic potash.

D. A. L.

**Estimation of Chlorine, Bromine, and Iodine in Presence of one another.** By F. M. LYTE (*Chem. News*, **49**, 4).—It has been shown (this vol., 393—394) that bromine decomposes silver chloride, and that iodine decomposes silver bromide. The author now communicates a convenient method of applying these reactions for quantitative purposes. The silver precipitate, containing all the halogens, is dried, weighed, and then dissolved in 30 to 40 times its weight of water, by adding the smallest possible quantity of potassium cyanide. A quantity of potassium bromide equal in weight to the precipitate is now added, and the cyanide decomposed by excess of dilute sulphuric acid. The precipitate which contains bromide and iodide (any chloride being now bromide) is dried, weighed, and then redissolved as before. One and a quarter times the weight of the original precipitate of potassium iodide is now added, the cyanide decomposed as

above, and the precipitate dried and weighed. The quantity of chlorine, bromine, and iodine present is easily calculated from the differences in the weights of the three weighings. D. A. L.

**Improved Form of Orsat's Apparatus for the Estimation of Oxygen.** By J. B. C. KERSHAW (*Chem. News*, 49, 73—74).

**Volumetric Estimation of Potash.** By E. MARCHAND (*Ann. Agronomiques*, 9, 465—469).—The basis of this method is the diminution of acidity caused by the separation of insoluble hydrogen potassium tartrate from a mixture of sodium hydrogen tartrate with a neutral solution of a potassium salt.

*Standard sodium hydrogen tartrate* is prepared of such a strength that 1 c.c. will precipitate 10 mgrms. of potash ( $K_2O$ ): 40 c.c. of this solution are added by means of a pipette to 10 c.c. of a carefully neutralised solution containing 0.5 gram of the potash salt to be tested. The mixture is left at rest during the night, and a similar flask containing 50 c.c. of water is placed beside it. The bulb of a minimum thermometer is plunged in the water of the second flask, and the lowest temperature reached is noted in the morning. A solution of cochineal containing 0.1 gram per litre is used as indicator, and the 10 c.c. of the mother-liquor from which the cream of tartar has separated are diluted with the coloured liquid to 30 or 40 c.c., and titrated with standard alkali delivered from a 10 c.c. burette graduated to  $\frac{1}{10}$  c.c., but so narrow that  $\frac{1}{100}$  c.c. may be judged by the eye (1 c.c. occupies about 3 cm. of this burette). The burette is drawn out to a capillary jet at the lower end, and is furnished with a stopcock at its upper end, being filled by suction through a caoutchouc tube attached above the stopcock.

The quantity of standard alkali consumed being accurately noted, the required percentage of potash is found by reference to a table opposite the minimum temperature at which the potassium hydrogen tartrate was deposited. Thus, if the acidity of the 40 c.c. of standard sodium hydrogen tartrate is lowered in an experiment from 8.00 c.c. standard alkali to 2.79 c.c., with a minimum temperature of 9°, the percentage of potash in the salt examined is found to be 56.3. If under the same circumstances the minimum temperature were 14°, the percentage would be 58.8. This method is applicable in presence of sodium, calcium, and magnesium salts, and succeeds equally well with the chloride, nitrate, or sulphate of potassium. Ammonium salts must of course be absent. The standard sodium hydrogen tartrate may be preserved indefinitely by addition of a little camphor, if kept in the dark. The empirical table referred to above is not yet published. J. M. H. M.

**Volumetric Estimation of Mercury.** By G. KROUPA (*Chem. News*, 49, 14).—Recently precipitated mercurous chloride is readily converted into sulphide and hydrochloric acid by means of hydrogen sulphide solution, therefore by determining the chlorine in solution the quantity of mercury present can be calculated. With mercuric

salts, when required, a sufficient quantity of sodium chloride is added, then a solution of ferrous sulphate and potash. The mixture is well stirred, and after a few minutes is strongly acidified with dilute sulphuric acid. The mercurous chloride thus obtained or that precipitated direct from mercurous salts, is filtered, washed, and with the filter placed in and covered with hydrogen sulphide solution. The hydrochloric acid produced is neutralised with barium carbonate, the excess of hydrogen sulphide got rid of by means of zinc acetate, the zinc sulphide filtered off, well washed, and the chlorine titrated in the filtrate.

D. A. L.

**The Ammonia Process for Water Analysis.** By N. H. DARTON (*Chem. News*, 49, 65—67).—In the ordinary course of water analysis, the non-ammoniacal volatile nitrogenous (organic) matters are not estimated, because they do not act on Nessler solution. The author determines this amount of nitrogen by dividing the distillate for ammonia-testing into two equal parts; the one part he Nesslerises in the ordinary manner, the other he distils with ammonia-free alkaline potassium permanganate and Nesslerises the distillate; the difference between the two Nessler testings is due to the volatile organic nitrogenous matter decomposed during the second distillation. The author considering this to be of great importance, has examined the physiological action of the concentrated volatile nitrogenous organic matter obtained from various pump-waters from the cities of New York and Brooklyn; these waters are well polluted, and contain plenty of these nitrogenous matters. He finds that when injected under the skin of rabbits, the concentrated nitrogenous matters generally produce unpleasant symptoms, mostly of diarrhœa, sometimes accompanied by vomiting, and frequently followed by death. By subsequent experiments, he shows that these effects are really due to the matters in question, and accounts for their varying in action by assuming that these volatile matters include both virulent and harmless amine-compounds. The following is the manner of concentrating these matters:—5 litres of water are distilled in half litres at a time, collecting in each case 100 c.c.; the litre of combined distillates is subjected to similar treatment, and the two 100 c.c. thus obtained are mixed, treated with the calculated quantity of phosphoric acid to fix free ammonia, distilled, and 50 c.c. of distillate collected, and after redistilling, is found to be free from ammonia. In this way two-thirds (of the amount found by analysis) of the ammonia of the volatile nitrogenous matter is obtained, other bodies, chemical and organised, being left behind. In some injection experiments the original waters were found to produce symptoms similar to those induced by the concentrated, thus supporting the suggestion of the pre-existence of those substances in the waters.

D. A. L.

**Estimation of Tannin in Vegetable Products.** By M. PERRET (*Chem. News*, 49, 52).—In the process recommended, the clear aqueous extract of the substance under examination is concentrated, and while warm is mixed with a measured quantity of solution of egg-albumin in excess, heated to 100°, decinormal aluminium sulphate

is then run in from a burette until the deposit becomes granular and settles down. This is filtered on a tared filter, washed, dried, and weighed. The weight of the tannin is obtained by deducting the weight of the albumin and aluminium sulphate added, as well as the weight of the filter-paper from the total weight.

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D. A. L.

## Technical Chemistry.

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**Coal-gas as a Source of Heat.** By T. FLETCHER (*Chem. News*, 49, 74—86).

**Zinc in Drinking Water.** By C. W. HEATON (*Chem. News*, 49, 85).—Water from a spring at Penderry of the composition given below was passed for about half a mile through a galvanised iron pipe, with the following result :—

Constituents.	Grains per gallon.	
	Spring.	Pipe.
Total solids .....	10·80	18·90
Chlorine .....	1·47	1·45
Ammonia .....	none	0·008
Nitrogen as nitrate .....	0·056	none
Zinc carbonate in solution in carbonic acid .....	none	6·41

This result was confirmed in a subsequent experiment, when the solution of the zinc was effected by passing a stream of oxygen and carbonic anhydride for half an hour through distilled water containing fragments of the pure metal. The author remarks on the reduction of nitrates to ammonia by the action of zinc.

D. A. L.

**Use of Carbolic Acid in the Disinfection of Sewage.** By O. KELLNER and others (*Landw. Versuchs.-Stat.*, 30, 52—58).—During a cholera epidemic in Japan, 1882, the Government ordered that all human excrement should be treated with carbolic acid and ferrous sulphate. This description of manure is that most largely used in Japanese agriculture, and when the farmers refused to purchase, fearing to injure their crops by the disinfectants, it became a serious matter for both towns and country. With a view of learning whether the use of carbolic acid was really hurtful to growing crops, the Government ordered experiments to be made at their experimental farm. The mode of cultivation in Japan is particularly adapted to show injurious properties in the manure if it possessed any, as the manure is spread, or distributed if fluid, immediately before sowing, and the seeds put in immediately. The experiment consisted in steeping a number of seeds for a certain time in solutions of carbolic acid of different strengths, then placing them between filter-paper in

covered beakers until germination took place, the papers being frequently moistened with the proper solution. Parcels of 200 seeds each, of *Phaseolus radiatus*, were placed for 42 hours in 100 c.c. of the following concentrations and inspected at regular periods.

Experiment .....	1.	2.	3.	4.	5.	6.
Per cent. carbolic acid ..	0	0·025	0·05	0·10	0·15	0·20
Hours after steeping.	Number of seeds germinated.					
48	40	34	21	0	—	—
72	52	43	30	8	—	—
96	38	44	52	6	—	—
120	13	22	28	2	—	—
144	8	6	10	6	—	—
168	5	15	13	4	—	—
192	17	10	12	10	—	—
8 days	173	174	166	36	—	—
Per cent. ....	86·5	87	83	18	—	—

According to these figures, a solution of 0·05 of carbolic acid in 100 c.c. water clearly weakened the germinating power of the seeds, and with a solution of 0·1 per cent. only one-third of the possible seeds germinated, and in all cases the acid delayed the process of germination. A second series of experiments was made with wheat, the results being similar, the acid in all cases delaying germination. Field experiments were then undertaken, and the injurious effects of the disinfected manure showed in the growth of wheat and barley when the land was cultivated in the manner usual in Japan, but when the manure was applied earlier, for example in October, ploughed in and left to the rains of winter, the author thinks the carbolic acid was carried into the subsoil out of the reach of the roots. Wheat, barley, and buckwheat behaved in a similar manner, the injurious effects of the acid being but feebly apparent when the manure was applied early.

J. F.

**Formation of Sulphuric Acid in the Lead Chambers.** By G. LUNGE (*Chem. News*, 49, 13—14).—This communication is based on results of observations made in a works in Switzerland. Firstly, with regard to *nitrogen peroxide*; as this substance takes no part in the formation of sulphuric acid, its presence is not necessary in the lead chambers; in fact, it is only a secondary product formed under special conditions. For example, it is produced in the last chamber when there is a large excess of nitrous gas, and where the quantity of sulphuric acid formed is small. Its production is apparently greatly favoured by absence or reflux of sulphurous acid, whilst it is not affected by the amount of oxygen present. Nitrogen peroxide is



never found in tower acid (compare Abstr., 1882, 1010, 1162). When the gaseous mixture in the chambers is yellow, there is considerable loss in nitrous anhydride and nitrogen peroxide in the Guy-Lussac tower, when, on the other hand, it is colourless, the loss as nitrate is great, and the escaping gases contain nitric oxide, sulphurous anhydride, and only traces of the above gases. The *oxidation of sulphurous anhydride* goes on rapidly at first, 75 per cent. is converted into sulphuric acid by the time the gaseous mixture has reached the centre of the first chamber; only 4 per cent. more undergoes conversion from the centre to the end of this chamber, whilst 10 per cent. is changed in the pipe connecting chambers 1 and 2. The employment of a series of several chambers connected by small pipes is very favourable to the good working of a plant; the pipes seem to effect the compression, and therefore the more intimate mixture of the gases. The *mixture of the gases* is complete in the centre of the first chamber (compare Abstr., 1883, 129), the composition being constant at different heights, there is, however, in the centre from 0.1 to 0.2 per cent. more sulphurous anhydride than along the sides. The *temperature* rises  $5^{\circ}$  to  $6^{\circ}$  in the first quarter of the first chamber, and then falls slowly, the decrease becoming stronger towards the end of the series of chambers. In the middle of first chamber, the temperature at the bottom is  $5^{\circ}$  lower than at the top. The temperature is about the same whether steam or water spray is employed. Increasing the size of chambers for the same quantity of sulphur causes a diminution of temperature. The *cooling effect of the sides of the chambers* scarcely penetrates more than 25 cm. into the interior, for example: external temperature being  $19^{\circ}$ , at 5 to 10 cm. from the side reduction of temperature is  $2^{\circ}$ , at 10 to 25 cm. only  $1^{\circ}$ ; whilst from 25 cm. (from side) to centre of chamber difference is  $5^{\circ}$ , and from side to centre  $8^{\circ}$ .

D. A. L.

**Barium and Strontium in a Boiler Incrustation.** By C. L. BLOXAM (*Chem. News*, 49, 3).—The incrustation examined was deposited in a kitchen boiler from water from a deep chalk well in Harrow, which contained, in grains per gallon, 14.48  $\text{SO}_3$ , 8.88 Cl, 7.21 CaO (SrO, BaO), 5.61  $\text{MgO}$ , 15.20  $\text{Na}_2\text{O}$ , 12.60  $\text{CO}_2$  (combined), 1.28  $\text{SiO}_2$ . The deposit contained only a small quantity of barium sulphate, but 1.54 per cent. of strontium sulphate. The precipitates of both these metals were examined spectroscopically.

D. A. L.

**Sorgho-sugar Making in America.** By G. DUREAU and PELLET (*Bied. Centr.*, 1883, 788).—The yield of sap from 100 kilos. sorgho-stalk is 65 kilos., containing 12.5 per cent. crystallisable sugar, and 3.7 per cent. molasses. Pellet finds in raw sorgho-sugar 92 per cent. sugar and 2.56 per cent. glucose.

J. K. C.

**Composition of Residues obtained in the Beet-sugar Manufacture.** By A. PAGNOUL (*Bied. Centr.*, 1883, 789).—In fresh residues, the sugar varies from 6.5 to 0.48 per cent., the former being obtained from the hydraulic press, and the latter by maceration; the percentage of nitrogenous substance varies from six in the former to twelve in

the latter. Similar differences are observable in the residues which have been kept.

J. K. C.

**Russian Cheese.** By A. KALANTAROFF (*Bied. Centr.*, 1883, 719).—Five analyses are given as follows:—

Constituent.	1.	2.	3.	4.	5.
Water.....	29·80	32·51	35·44	34·68	31·26
Fat .....	37·20	29·68	28·97	32·53	32·94
Albuminoids .....	20·57	26·16	28·81	24·15	24·54
Ash.....	5·96	7·44	6·21	4·92	4·36
Non-nitrogenous matter and loss .....	6·74	4·21	0·57	3·72	6·90
Per cent. sodium chloride { in cheese..	2·41	4·78	3·09	1·63	1·45
in ash ....	42·35	64·25	49·76	33·13	32·26

D. A. L.

**Action of Aluminium Sulphite on Manganic Hydroxide.** By G. SCURATI-MANZONI (*Gazzetta*, 13, 567).—It is well known that stannous chloride converts manganic hydroxide into soluble manganous chloride, and is itself converted into insoluble stannic acid—a reaction which is utilised for facilitating the fixation of certain colours on cotton and wool fibres, the stannic acid acting as a mordant. Now, aluminium sulphate acts in exactly the same way, giving rise to soluble manganous sulphite and insoluble aluminium hydroxide, which is deposited on the fibre, and renders it capable of receiving a dye. In the bleaching of textile fibres with potassium permanganate, the cleansed or scoured fibres are coloured brown by the manganic hydroxide produced, and require to be bleached by sulphurous acid. Now, by employing aluminium sulphite instead of sulphurous acid, the bleaching and aluming of the fibres may be effected in one and the same operation.

H. W.

**Action of Sunlight, Daylight, and Electric Arc Light on Water and Oil Colours used in Dyeing and Painting.** By M. DECAUX (*Chem. News*, 49, 51).—The colours in wool dyed in the vat with Prussian blue, cochineal, madder, weld, and fustic, are more permanent than those obtained with Nicholson blue, magenta, jaune d'or, and picric acid. Naphthol carmine, orange No. 2, chrysoidine, and artificial alizarin, are more stable than other coal-tar colours. Pigments are divided into permanent, moderately permanent, and fugitive. Used with water, all the most beautiful reds, carmine, carmine lake, most madder lakes, and vermilion are classed as fugitive. With oil, madder lakes are moderately permanent. The electric arc light acts like sunlight, but with one-fourth the power.

D. A. L.

## General and Physical Chemistry.

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**Absorption Spectrum of Water.** By J. L. SORET and E. SARASIN (*Compt. rend.*, **98**, 624—626).—A beam of light passed through a thickness of 2·2 metres of water shows a faint and narrow absorption-band in the orange at about wave-length 6000. With a thickness of 3·3 metres, this band is slightly more distinct and there is general absorption of the extreme red, and with a thickness of 4·5 metres the absorption-band is darker, but still remains faint, and the general absorption in the red is increased. This absorption-band is observed with water from different localities, with ordinary distilled water, and with most carefully purified distilled water, and it must therefore be due to the water itself and not to any substance dissolved in it.

Even with a thickness of 8 metres, the authors were unable to distinguish the absorption-band between *a* and *b* seen by Vogel in the light in the grotto of Capri, hence it would seem that this band is due to some substance in solution in sea water. C. H. B.

**Influence of the Chemical Nature and Pressure of Gases on the Generation of Electricity by an Induction Machine.** By W. HEMPEL (*Ber.*, **17**, 145—148).—A Töpler's induction machine was so arranged in a glass case, that it could be worked in an atmosphere of gas at any required pressure. The results showed that with air at 2 atmospheres pressure, an amount of electricity was developed about twice as great as at 1 atmosphere pressure under like conditions, whilst on diminishing the pressure to  $\frac{1}{2}$  atmosphere, scarcely any electricity was generated. With regard to the influence of different gases, it was found that on working under like conditions in hydrogen, air, and carbonic anhydride, the quantities of electricity obtained had the ratios 9 : 45 : 47. A. J. G.

**The Clausius-Williamson Hypothesis.** By S. ARRHENIUS (*Ber.*, **17**, 49—52).—This is a reply to Jahn (*Ber.*, **16**, 2449) in defence of the above hypothesis.

**Freezing Point of Solutions of Salts of the Alkali-metals.** By F. M. RAOULT (*Compt. rend.*, **98**, 509—512. Compare *Abstr.*, 1883, pp. 7, 278, 952, and this vol., 254).—The author has extended his researches to solutions of various salts of the alkali-metals. The results are given in tables, and the salts employed are divided into five groups. The first group consists of normal or acid salts which contain one atom of the alkali-metal, and in this group the molecular reduction of the freezing point varies between 27 and 36, the mean being 32. Normal salts of oxyacids give a reduction approaching 31; normal salts of hydracids give a reduction approaching 35. The rare instances in which the reduction approaches 27 are di-acid salts, which are partially decomposed by water. The second group

consists of salts which contain two atoms of the metal; the molecular reduction is about 40. Salts containing three atoms of the metal give a molecular reduction of about 48, but this number is somewhat too high, because these salts are partially decomposed by water. Salts which contain four atoms of the metal, *e.g.*, pyrophosphates and ferrocyanides, produce a molecular reduction of about 47. The fifth group contains potassium ferricyanide and cobaltcyanide, which are regarded as containing six atoms of the base in the molecule. The molecular reduction is about 96, a number which is quite abnormal, and indicates that the molecular weight ascribed to these salts is, when they are in solution, double the true molecular weight.

C. H. B.

**Law of Thermo-Chemical Moduli or Constants of Substitution.** By BERTHELOT (*Compt. rend.*, 98, 400).—The author shows that this law is altogether inapplicable to soluble salts of mercury. Tommasi considers, however (*ibid.*, 637), that the heats of formation of these salts have not yet been determined with sufficient accuracy.

C. H. B.

**Absorption of Gases of Platinum.** By BERTHELOT (*Ann. Chim. Phys.* [5], 30, 519—538).—A study of the phenomenon of electrolytic polarisation induced the author to investigate the heat changes involved in the absorption of gases by platinum. Three forms of the metal were used, *viz.*, platinum-dust, metal reduced by formic acid, and platinum-black; the action on them of oxygen and hydrogen was studied. The method of investigation is also given in detail.

*Platinum-dust.*—From the experimental results it is deduced that for every gram of hydrogen absorbed by the dust and susceptible of oxidation in the cold by oxygen, heat is developed 9.5 cal.

*Metal Reduced by Formic Acid.*—This form seems to combine with hydrogen in two successive stages, one hydride being oxidised by oxygen in the cold, but the other only at high temperatures. The results were as follows:—

	Cal.
1. Formation of hydride saturated with hydrogen, $Pt_x + H_3 = Pt_xH_3$ .....	+ 42.6
2. Formation of the same from an unsaturated hydride, $Pt_xH_2 + H = Pt_xH_3$ .....	+ 8.7

Therefore

3. Formation of the unsaturated hydride from its elements $Pt_x + H_2 = Pt_xH_2$ .....	= 33.0
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In the production of this latter 17.0 cal. are developed for every equivalent of hydrogen. The value for *x* in the above formulæ is approximately 60; the formula of the hydrides is thus  $Pt_{60}H_3$  and  $Pt_{60}H_2$ .

*Platinum-black.*—The results obtained with this form are not sufficiently definite, the phenomenon being complicated by the presence of some suboxide, which absorbs and reacts with the hydrogen.

**Absorption of Oxygen.**—The quantity of heat developed in the absorption of oxygen by platinum is very small, and the results here

adduced are probably too high. The relative volume of the oxygen absorbed to the platinum is too small for calculation.

Form of metal.	Weight of metal.	Heat developed.
Platinum-dust .....	117.6	0.0083 cal.
Platinum reduced by formic acid .....	66.3	0.0094 „
Platinum-black .....	—	0.0180 „

As regards the last results, it was observed that the heat developed was diminished each time that the metal was heated to 200° in a vacuum; this diminution seems to point to a change in state of the platinum-black on heating.

These investigations show that the electromotive force required to decompose water in the presence of platinum is equivalent to the difference between the heat changes corresponding with the separation of hydrogen and oxygen (+ 34.5 cal.), and the sum of the heat changes corresponding to the formation of the first hydride (+ 17 cal.) and of the suboxide of platinum. This last factor is unknown, but is doubtless considerable. The energy necessary for the change is present in the system at the commencement of the reaction, but is arrested temporarily by the chemical changes supervening on the surface of the platinum.

The phenomenon of the so-called spontaneous combustion of hydrogen and oxygen in presence of platinum can also be explained by the aid of these researches; at first the unstable hydride of platinum is formed, with development of heat, and this is oxidised by the oxygen with a still further development of heat. By a continued repetition of the above changes, the platinum is raised to the temperature necessary for the ignition of the gaseous mixture. This explanation conforms to the observed succession of phenomena.

V. H. V.

**Reciprocal Displacements of Hydrofluoric Acid and other Acids.** By BERTHELOT and GUNTZ (*Compt. rend.*, 98, 395—399).—A comparison of the quantities of heat developed in each of the four reactions which may take place between hydrofluoric and hydrochloric acids and the corresponding potassium salts, shows that in every case the maximum thermal effect corresponds with the formation of potassium hydrogen fluoride, and this conclusion is verified by experiment. If a current of dry hydrochloric acid gas is passed over dry potassium fluoride at the ordinary temperature, the hydrochloric acid is absorbed, and potassium chloride and potassium hydrogen fluoride are formed, but no hydrofluoric acid is given off. If, however, the substances are heated, the acid fluoride decomposes into hydrofluoric acid, which is given off, and the normal fluoride. The latter is converted by a further quantity of hydrochloric acid into the chloride and acid fluoride; this acid fluoride is in its turn dissociated, and the same series of changes goes on until the whole of the fluoride is converted into chloride. In the same way, when dry hydrofluoric acid gas acts on potassium chloride in the cold, hydrochloric acid is

given off, and potassium hydrogen fluoride is formed, but at a moderately high temperature the chloride is gradually converted into the normal fluoride.

If these substances are in solution, the base is unequally divided between the two acids, as Thomsen has previously shown, but the authors regard this result as due entirely to the formation of potassium hydrogen fluoride and its partial dissociation in presence of water, and not, as Thomsen supposes, to a special coefficient of affinity proper to each acid. The results of experiment are in complete agreement with the deductions from thermochemical data: whether the substances are solid or in solution, the maximum thermal effect corresponds with the formation of the acid fluoride.

Precisely similar results are obtained with nitric acid: in the case of sulphuric acid, an acid sulphate and an acid fluoride are first formed, but are afterwards decomposed by heat.

In the case of acetic acid, thermochemical data indicate that the base will be divided between the two acids, and this is confirmed by experiment. The partial displacement of hydrofluoric acid by acetic acid is due to the formation of the acid fluoride. Oxalic and tartaric acids, whether solid or in solution, behave in a similar manner, the acid fluoride being formed together with the acid tartrate or oxalate as the case may be.

Similar considerations indicate that hydrofluoric acid should be partially displaced by hydrocyanic acid, and it is found that at a dull red heat there is a sensible displacement of hydrofluoric acid, with formation of potassium cyanide. In the cold the same change also takes place, but more slowly. Inversely, hydrofluoric acid decomposes potassium cyanide with formation at first of the acid fluoride.

C. H. B.

**Hydrogen Potassium Fluoride in Solution.** By GUNTZ (*Compt. rend.*, **98**, 428—431).—The proportion of hydrogen potassium fluoride existing in a solution is diminished by dilution, but increases with an increase in the proportion of hydrofluoric acid. When the normal potassium fluoride is added to a solution of hydrofluoric acid, the amount of acid fluoride formed increases with the proportion of normal fluoride. The conditions of equilibrium are analogous to those observed by Berthelot and Péan de Saint-Gilles in the formation of ethers; in both cases, the effect of the acid is greater than that of the other compound (normal salt or alcohol).

For the degree of dilution employed in these experiments (1 gram-equivalent in 2 kilos.), the amount of dissociation is twice as great in a solution containing equal equivalents of the normal salt and acid, as in a solution containing a large excess of normal salt, and two and a half times as great as in a solution containing a large excess of acid.

C. H. B.

**Double Salts formed by Fusion.** By BERTHELOT and LOSVAY (*Ann. Chim. Phys.* [5], **29**, 295—342).—This paper contains an account of the study of the thermal phenomena attending the production by fusion of a large number of double salts.

The method of investigation consisting in the determination (1) of the heat of solution of the simple salts used; (2) of the heat of solu-

tion of the same after fusion; (3) the heat of solution of the double salts immediately after preparation, and also after keeping for some time. The results obtained have enabled the authors to draw the following conclusions. A large number of double salts can be prepared by fusion, such as double chlorides, chlorobromides, double carbonates, and double sulphates, which retain even at the ordinary temperature a positive heat of formation; these form stable compounds, and may also be prepared in the wet way. On the other hand, the heat of solution of some systems of double salts is greater than the sum of those of their constituents. The instability of these systems is shown by this difference gradually decreasing after the double salts have been kept for some time. Further, the heat disengaged when a system assumes its final state becomes less as a rule in the case of simple salts than in that of systems formed by the fusion of two mixed salts, which, in all probability, may be due to the existence at the temperature of fusion of the double salts belonging to the same chemical types as the double chlorides, chlorobromides, double sulphates, and double carbonates. Such are the double chlorides of potassium, and of sodium, or of barium, or strontium, &c.: compounds becoming endothermic in cooling, but which are analogous to the double chlorides of potassium and of magnesium, or of calcium, the formation of which remains exothermic in the cold. So also the chlorobromide, chloriodide, and iodobromide of potassium are endothermic compounds in the cold, but are analogous to the chlorobromide of barium, which remains exothermic in the cold. In like manner the double sulphates of potassium, of sodium, or of barium, or of strontium, are endothermic in the cold, although they are analogous to the double sulphates of magnesium, the formation of which remains exothermic in the cold. A similar instance is found in the case of the double carbonate of potassium and barium, which is endothermic in the cold, but is analogous to the double carbonate of potassium and sodium. The authors point out that it is quite possible that the association of two simple salts may give rise to combinations which remain exothermic at the ordinary temperature, whilst other combinations differing in the relative amounts of the constituents become endothermic in the process of cooling. The double carbonate of potassium and sodium exhibits the same phenomenon.

The systems  $\text{K}_2\text{CO}_3 + \text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3 + 2\text{Na}_2\text{CO}_3$ , and  $2\text{K}_2\text{CO}_3 + \text{Na}_2\text{CO}_3$ , become exothermic from the first moments of cooling. The following,  $\text{Na}_2\text{CO}_3 + 3\text{K}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3 + 5\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3 + 4\text{K}_2\text{CO}_3$ , become exothermic after some time, and finally the system  $\text{K}_2\text{CO}_3 + 4\text{Na}_2\text{CO}_3$  remains endothermic to the end of two months. Some double salts in the anhydrous state are endothermic at the ordinary temperature, but may become exothermic by the aid of water of crystallisation; again, the formation by fusion of the double anhydrous salts may be attended with development of heat. The double salts of the different kinds just described play a very important part in many reactions and metamorphoses produced in the dry way.

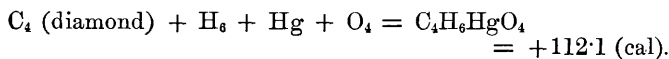
As, for instance, the crystallisation of barium sulphate and strontium sulphate from their double sulphates. Barium carbonate

also crystallises at the expense of the fusible double carbonate containing it. The crystalline silicates formed by the devitrification of glass, the formation of corundum, ruby, and the crystalline silicates, as obtained by Fremy and Feil, are all formed under conditions of the same order; in other words, double salts are first formed by fusion, from which their components separate in the crystalline state by the dissociation and final decomposition of the double salts, this decomposition taking place at times at the moment of solidification, at others slowly in the solidified mass, but never without a continuous and characteristic development of heat. The most important application of the existence of these double salts is to be found in their intervention in such double decompositions as that of barium sulphate by potassium and sodium carbonates by fusion. Reactions of this character are never complete, when equivalent quantities are used, requiring as they do for their completion an excess of the carbonates of the alkali-metals. The true reaction does not take place between four simple salts alone—such as barium carbonate and sodium carbonate, or barium sulphate and sodium sulphate; double carbonates of barium and of sodium, and double sulphates of barium and sodium are formed, the dissociation of which double salts results in the formation of the simple salts derived from them. If the latter be eliminated their formation becomes complete, if they remain in the presence of their components then their formation is limited in a definite manner by the dissociation of the double salts to an extent dependent on their relative proportions, the conditions regulating this species of reaction being exactly similar to those which obtain in reactions between salts in solution. In both cases, the equilibrium is effected by the intervention of secondary compounds existing in a state of partial decomposition.

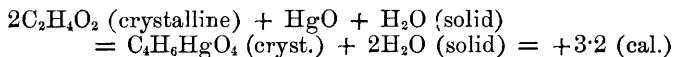
P. P. B.

**Some Mercuric Salts.** By BERTHELOT (*Ann. Chim. Phys.* [5], 29, 351—353).—Mercuric acetate,  $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$ , forms white well-defined crystals, is easily soluble in cold water, its solution decomposes on boiling or keeping with formation of basic salts. The heat produced by neutralising mercuric oxide by acetic acid was found indirectly to be 3.04 cal., and by direct experiment to be + 3.17.

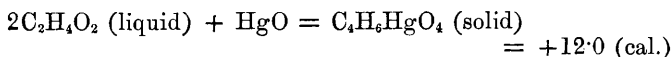
*Heat of Formation of Mercuric Acetate.*—(1.) From its elements—



(2.) Hydrated solid—



(3.) From anhydrous acid—

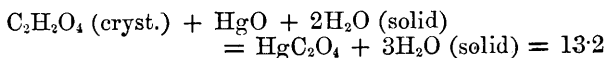


*Mercuric oxalate*,  $\text{HgC}_2\text{O}_4$ , is obtained by precipitating mercuric

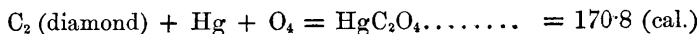


acetate with oxalic acid. The heat of neutralisation of mercuric oxide by oxalic acid is + 14.1 (cal.).

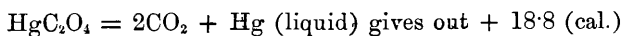
*Heat of Formation of Mercuric Oxalate in Solid State.*—(1.) From the acid and oxide—



(2.) From its elements—

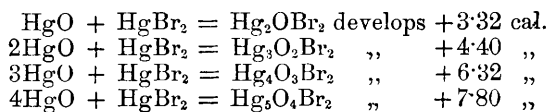


From this last number one can understand the explosive decomposition of mercuric oxalate, a phenomenon which may be easily produced by heat, as the following numbers show :—



P. P. B.

**Heat of Formation of Mercuric Oxybromides.** By G. ANDRÉ (*Compt. rend.*, 98, 515—516).—These compounds were obtained by heating mercuric bromide with the requisite quantity of red mercuric oxide in sealed tubes for six hours at about 300°. They are crystalline, of an iron-grey colour, and when treated with potash they yield yellow mercuric oxide. Their heats of formation were determined by dissolving them in an excess of hydrobromic acid, when the following results were obtained :—



These numbers are slightly lower than those for the corresponding compounds of lead, and also lower than those for the corresponding oxychlorides, except in the case of the first term of each series ( $\text{HgBr}_2, \text{HgO}$  and  $\text{HgCl}_2, \text{HgO}$ ), when the values are the same.

The author was unable to obtain in the wet way the oxybromide,  $3\text{HgO}, \text{HgBr}_2$ , described by Rammelsberg and Loewig. The product obtained by the action of sodium carbonate in varying proportions on an aqueous solution of mercuric bromide at different temperatures is the oxybromide  $4\text{HgO}, \text{HgBr}_2$ .

C. H. B.

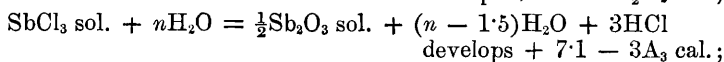
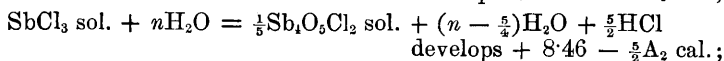
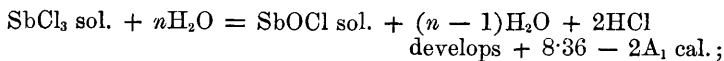
**Heat of Formation of Antimony Oxychlorides.** By GUNTZ (*Compt. rend.*, 98, 512—514).—*Antimony Chloride.*—The heat of formation was determined by dissolving the oxide in hydrochloric acid, and also by dissolving corresponding weights of the chloride and oxide respectively in very dilute hydrofluoric acid, and comparing the thermal effects. The mean result obtained was  $\text{Sb}_2\text{O}_3$ , prismatic, anhydrous, +  $6\text{HCl}$  gas =  $2\text{SbCl}_3$ , solid, +  $3\text{H}_2\text{O}$ , solid, develops + 94.8 cal.

*Antimony Oxychloride*,  $\text{SbOCl}$ .—This compound was obtained by decomposing 10 parts of the chloride with 7 parts of cold water, and its heat of formation was determined by dissolving in dilute hydro-

fluoric acid as in the case of the chloride:  $\text{Sb}_2\text{O}_3$ , prismatic, +  $2\text{HCl}$ , gas, =  $2\text{SbOCl}$ , solid, +  $\text{H}_2\text{O}$ , solid, develops + 38·8 cal.

*Antimony Oxychloride*,  $\text{Sb}_4\text{O}_5\text{Cl}_2$ .—This compound was obtained in triclinic prisms by decomposing the chloride with its own weight of water at  $250^\circ$ , and the heat of formation was determined as in the previous cases.  $2\text{Sb}_2\text{O}_3$ , prismatic, +  $2\text{HCl}$ , gas, =  $\text{Sb}_4\text{O}_5\text{Cl}_2$ , solid, +  $\text{H}_2\text{O}$ , solid, develops + 41·2 cal.

From these numbers it follows that—



where  $A$  is the heat developed by the dilution of one equivalent of hydrochloric acid by a large quantity of water. The maximum thermal effect corresponds with the formation of the oxychlorides, and if  $A$  is relatively considerable, and if  $8\cdot36 - 2A > 8\cdot46 - 2\cdot5A_2$ , the maximum thermal effect corresponds with the formation of  $\text{SbOCl}$ . Since, however, the state of dissociation of the hydrates in the liquid is not known, the value of  $A$ , and consequently the value of  $n$ , cannot be accurately calculated. The order of the reaction will, however, be first the formation of the oxychloride,  $\text{SbOCl}$ , and afterwards the production of the compound,  $\text{Sb}_4\text{O}_5\text{Cl}_2$ . These conclusions agree with Sabanejeff's observations.

The author criticises Thomsen's previous determinations of the heats of formation of the compounds. C. H. B.

**Density of Metals in the Liquid State.** By W. C. ROBERTS and T. WRIGHTSON (*Ann. Chim. Phys.* [3], **30**, 274—288\*).—In this memoir are collected together the results of the authors' investigations on the density of metals in the liquid state by the "oncosimeter" method; these are compared with those obtained by Mallet's cone method.

Metal.	Density of liquid metal.		Density of solid metal.	Percentage change of volume.
	By cone method.	By oncosimeter method.		
Bismuth .....	10·039	10·055	9·82	— 2·30
Copper .....	—	8·217	8·80	+ 7·10
Lead .....	10·650	10·370	11·40	+ 9·93
Tin .....	6·994	7·027	7·50	+ 6·76
Zinc .....	6·550	6·480	7·20	+ 11·10
Silver .....	9·400	9·510	10·57	+ 11·20
Iron .....	—	6·880	6·95	+ 1·02

\* By a printer's error this is paged 174—188.

As the errors involved in this process are inappreciable, the results may be considered sufficiently final. The objections brought forward against the process, viz., that the floating metallic ball may be of bad quality or form, and that the dilatation of the ball at the moment of immersion may cause an internal pressure within the ball, are met and discussed. The first source of error is completely avoided, and secondly the determination of the density of the liquid metal is inscribed automatically and at once before the volume of the ball can be appreciably modified. Since some of these results were published, Nies and Winkelmann have carried on investigations in the same direction, but by a different process (*Abstr.*, 1883, 545); these results show that the eight metals examined by them are less dense in the solid state, and at a temperature near their point of fusion than when they are melted. The aim of the authors' experiments was to determine the actual density of the metals at the lowest temperature at which they remain perfectly liquid. V. H. V.

**Melting Points of Haloïd Salts in Relation to the Contraction occurring during their Formation from their Elements.** By W. MÜLLER-ERZBACH (*Ber.*, 17, 198—200).—From a comparison of the melting points of the haloïd compounds of certain metals, as determined by Carnelley and Williams (*Trans.*, 1879, 563), with the theoretical melting points, as calculated by the formula

$$t = \frac{s_1 v_1 w_1 + s_2 v_2 w_2}{v_1 w_1 + v_2 w_2}$$

(in which  $s$  = melting point,  $v$  the combining weight, and  $w$  the specific heat of the element), the author deduces the rule: That for the haloïd salt of each element, the greater the difference between the found and calculated melting points, the greater the contraction occurring during the formation of the salt from its elements.

A. J. G.

**Gaseous Explosive Mixtures.** By BERTHELOT and VIEILLE (*Compt. rend.*, 98, 545—550, and 601—606).—By measuring the displacement of a piston of known section and mass, the authors have determined the pressures developed by the explosion of a large number of gaseous mixtures in closed vessels. In these two papers, tables are given showing the observed pressures, and the maximum and minimum limits of temperature, dissociation, and apparent specific heat calculated from the pressures by the methods previously described (*Abstr.*, 1883, 771). The discussion of these values is reserved for subsequent papers. C. H. B.

## Inorganic Chemistry.

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**Chlorine Monoxide for Lecture Experiments.** By V. MEYER (*Ber.*, 17, 157).—Chlorine monoxide requires a rather lower temperature for its liquefaction than that usually given. This is best effected by passing the gas through a Y-tube, the upper part of which is surrounded by alcohol that has been cooled to  $-40^{\circ}$  in a small ice machine. The liquefied monoxide can be collected in small test-tubes, cooled with a mixture of ice and salt, and placed below the lower limb of the Y. A few drops only should be collected in each tube.

A. J. G.

**Action of the Silent Discharge on Oxygen and Nitrogen in Presence of Chlorine.** By P. HAUTEFEUILLE and J. CHAPPUIS (*Compt. rend.*, 98, 626—627).—A mixture of pure chlorine and pure oxygen can be subjected to the action of the silent discharge without undergoing any alteration, but if nitrogen is also present, a white solid substance is deposited on the walls of the tube, and as the passage of the discharge is continued this deposit increases, and eventually assumes arborescent forms resembling ice crystals. This solid substance has practically no vapour-tension at  $15^{\circ}$ , but it readily volatilises in a vacuum at a moderate temperature, and can thus be purified from admixed foreign matter. It remains unaltered at  $100^{\circ}$ , but at  $105^{\circ}$  it rapidly decomposes without melting, and gives off nitrogen oxides. It rapidly absorbs moisture from the air, forming a strongly acid liquid, and when this is neutralised by potash or baryta the solution gives the reactions for nitrates and perchlorates. Analysis shows that it has the composition N, 9.01; Cl, 22.71; O (by diff.), 68.28 =  $\text{N}_2\text{O}_6\text{Cl}_2\text{O}_7$ .

It is probable that iodine and bromine form similar compounds under like conditions.

C. H. B.

**Carbonic Anhydride in the Atmosphere.** By A. MUNTZ and E. AURIN (*Ann. Chim. Phys.* [5], 30, 238—248). See this vol., p. 659.

**Sulphurous Anhydride in the Air of Lille.** By A. LADUREAU (*Ann. Chim. Phys.* [5], 29, 427—432). The amount of this gas in the air was determined by drawing a known volume of air through concentrated sulphuric acid, and then through vessels containing pure potassium hydroxide. The amount of sulphurous anhydride taken up by the potassium hydroxide was determined by converting it into sulphate, and estimating as barium sulphate. The results show the presence of 1.8 c.c. of this gas in 1 cm. of air; on calm days this amount was found to increase to 2 c.c., and to decrease to 1.4 c.c. on stormy days. The examination of carefully collected rain-water has shown it to contain sulphur compounds corresponding to 0.022 gram of sulphuric acid per litre.

The author observes that although the presence of this gas in the

atmosphere of towns such as Lille and other manufacturing towns, may be conducive to slight ailments of throat, &c., and minor inconveniences, still its antiseptic properties in case of epidemics compensate to a large extent for its evil effects.

P. P. B.

**Behaviour of Air and Moist Phosphorus towards Carbonic Oxide.** By I. REMSEN and E. H. KEISER (*Ber.*, **17**, 83—92).—The authors refer to their previous experiments (*Amer. Chem. J.*, **4**, 454; also this vol., p. 149) and to the opposite results obtained by Leeds (this vol., p. 15) and by Baumann (this vol., p. 14). They have repeated the experiment with a greater volume of air and with apparatus made wholly of glass, and their results show that under these conditions carbonic anhydride is actually produced when carefully purified air alone is employed and no carbonic oxide introduced. The formation of the carbonic anhydride is found to be due to the presence of carbon in the phosphorus (probably in combination), and the amount produced is distinctly influenced by the rate of the air current, by the temperature, and by the amount of phosphorus. Comparative experiments have also been made with and without carbonic oxide, and no difference could be detected in the amount of precipitation in the baryta solutions in the two cases. It is, therefore, inferred that carbonic oxide is not oxidised by air and moist phosphorus. The fact that the authors did not detect carbonic anhydride in their first experiments was due to the small volume of air employed.

A. K. M.

**Production of Crystalline Borates.** By A. DITTE (*Ann. Chim. Phys.* [5], **30**, 248—265).—On adding hydroxide or carbonate of the metal to a concentrated solution of boric acid, crystalline tetraborates of the general formula  $4B_2O_3, M''O, nH_2O$  are produced, provided the acid be in excess. On raising the temperature these salts are decomposed by water, half the boric acid going into the solution, with deposition of a biborate of the formula  $2B_2O_3, M''O, nH_2O$ . This result is only produced when the biborate crystallises from a small quantity of mother-liquor, for if the solution of the tetraborate be warmed and then allowed to cool, the inverse reaction is produced, and the biborate formed is reconverted into the tetraborate. The biborates in their turn are decomposed by pure water, provided that they are in the form of crystals or precipitates obtained by processes of double decomposition; they lose boric acid and are transformed into neutral borates of general formula,  $B_2O_3, M''O, nH_2O$ . The borates of these metallic oxides which form compounds with ammonia, give complex ammoniated borates, of which those of copper may be taken as typical:  $2B_2O_3, CuO, 2NH_4O$ . When heated these salts lose ammonia, and are converted into anhydrous borates in the form of amorphous powders. In the original paper, a full account is given of the various hydrated borates of the alkaline earths, magnesium, cadmium, zinc, nickel, cobalt, and silver. As regards the last-named, it has been observed by Rose that a concentrated solution of sodium biborate gives, with silver nitrate, a white precipitate of silver borate, but a dilute solution of the same salt gives a grey deposit of the oxide. In this paper, the changes produced by the successive additions of water to the pre-

precipitated silver biborate are minutely examined, and it is shown that the proportion of boric acid to silver diminishes as the water present is increased.

V. H. V.

**Preparation of Sodium Bicarbonate.** By H. GASKELL and F. HURTER (*Dingl. polyt. J.*, **251**, 228).—For the preparation of sodium bicarbonate, the authors subject the anhydrous normal carbonate to the simultaneous action of steam and carbonic anhydride. The apparatus employed consists of a rotary cylinder, similar in construction to that used by Carey.

D. B.

**Density of Milk of Lime.** By G. LUNGE (*Dingl. polyt. J.*, **250**, 464—466).—The author states that the table constructed by Mateczeck, showing the amount of lime in milk of lime of different strengths (*ibid.*, **215**, 72) is incorrect. He therefore gives the following values:—

*Table showing the Amount of Quicklime in Milk of Lime at 15°.*

Baumé.	1 litre of milk of lime weighs grams.	CaO in 1 litre, grams.	CaO per cent. by weight.	Baumé.	1 litre of milk of lime weighs grams.	CaO in 1 litre, grams.	CaO per cent. by weight.
1	1007	7·5	0·745	16	1125	159·0	14·13
2	1014	16·5	1·640	17	1134	170·0	15·00
3	1022	26·0	2·540	18	1142	181·0	15·85
4	1029	36·0	3·500	19	1152	193·0	16·75
5	1037	46·0	4·430	20	1162	206·0	17·72
6	1045	56·0	5·360	21	1171	218·0	18·61
7	1052	65·0	6·180	22	1180	229·0	19·40
8	1060	75·0	7·080	23	1190	242·0	20·34
9	1067	84·0	7·870	24	1200	255·0	21·25
10	1075	94·0	8·740	25	1210	268·0	22·15
11	1083	104·0	9·600	26	1220	281·0	23·03
12	1091	115·0	10·540	27	1231	295·0	23·96
13	1100	126·0	11·450	28	1241	309·0	24·90
14	1108	137·0	12·350	29	1252	324·0	25·87
15	1116	148·0	13·260	30	1263	339·0	26·84

It is useless to carry the table beyond 30° B., as in that case the milk of lime would become too thick.

D. B.

**Preparation of Strontia.** By H. NIEWERTH (*Dingl. polyt. J.*, **251**, 191).—The author mixes coelestin with equivalent quantities of coal and brown iron ore, and subjects the mixture to a roasting process. On lixiviating the roasted product with water, strontium hydroxide and iron sulphide are produced. Lead oxide or other metallic oxides can be used in the place of ferric oxide.

D. B.

**Barium Oxychloride.** By G. ANDRÉ (*Compt. rend.*, **98**, 572—574).—The author has previously described (*Abstr.*, 1881, 979) an

impure barium oxychloride, obtained by boiling barium oxide with a solution of barium chloride, and Beckmann (*Ber.*, **14**, 2151) has described a similar compound. If 200 grams of barium chloride are dissolved in 500 grams of boiling water, the solution allowed to cool slightly, 30 grams of finely powdered barium oxide added, and the mixture heated nearly to boiling for five minutes and then filtered, the filtrate on cooling deposits the oxychloride,  $\text{BaCl}_2 \cdot \text{BaO} \cdot 5\text{H}_2\text{O}$ , in nacreous lamellæ, free from excess of either barium oxide or chloride. If 60 grams of barium oxide are used instead of 30 (as originally described, *loc. cit.*), the filtrate at about  $60^\circ$  deposits the same nacreous lamellæ, containing, however, a slightly higher proportion of water, and if the liquid is quickly filtered when the temperature has fallen to  $50^\circ$ , the oxychloride is obtained in a state of purity, but if the liquid is allowed to cool further, large white lamellæ of barium hydroxide are deposited along with the oxychloride. C. H. B.

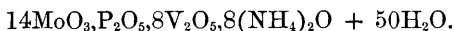
**Researches on the Complex Inorganic Acids.** By W. GIBBS (*Amer. Chem. J.*, **5**, 391—413).—A short notice of this subject has already been given (this vol., 161).

*Phospho-vanadio-molybdates.*—These salts are generally formed when phospho-vanadates are digested with molybdic tetroxide; when vanadio-molybdates and alkaline phosphates are heated together, especially in presence of an acid; and when vanadic pentoxide is heated with an alkaline phospho-molybdate. They are generally less stable than the vanadio-molybdates, yet well defined and usually highly crystalline; they are of an orange, deep garnet, or ruby-red colour.

Before determining the phosphoric acid by precipitation with magnesia mixture, it is necessary to remove vanadic oxide by boiling the slightly alkaline solution with a large quantity of ammonium nitrate, and after standing filtering off the ammonium metavanadate. By precipitation with mercurous nitrate and mercuric oxide, and ignition of the precipitate with sodium tungstate, the sum total of the acid oxides is determined, the molybdic oxide being then found by difference.

When the salt  $10\text{MoO}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 5(\text{NH}_4)_2\text{O} + 6\text{H}_2\text{O}$  and ammonium metavanadate are dissolved together, there appears to be no reaction, but if a small excess of hydrochloric acid be added, and the solution boiled, a deep orange-red crystalline precipitate is formed; it may be washed with cold water, but is decomposed by hot water; its composition is  $48\text{MoO}_3 \cdot 2\text{P}_2\text{O}_5 \cdot \text{V}_2\text{O}_5 \cdot 7(\text{NH}_4)_2\text{O} + 30\text{H}_2\text{O}$ .

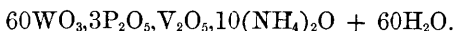
The phospho-molybdates of ammonium, containing  $24\text{MoO}_3 \cdot \text{P}_2\text{O}_5$  and  $22\text{MoO}_3 \cdot \text{P}_2\text{O}_5$ , slowly dissolve when boiled with a solution of ammonium metavanadate, and the solution after standing a few hours deposits deep ruby-red crystals. These may be recrystallised from hot water; the solution gives characteristic precipitates with several reagents. Analyses lead to the formula



If vanadic oxide be written  $\text{V}_2\text{O}_2\text{O}_3$ , and be regarded as standing in the same relation to phosphoric oxide as does molybdic oxide, then this salt belongs to the same type as the original phospho-molybdate,

viz.,  $22\text{MoO}_3, \text{P}_2\text{O}_5, x\text{R}_2\text{O}$ . Other salts are formed at the same time, but in small quantity only.

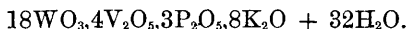
The *phospho-vanadio-tungstates* generally resemble and are prepared like the preceding salts. Phosphoric oxide is estimated by direct precipitation with magnesia mixture, but requires reprecipitation. Vanadic oxide is estimated by boiling with strong hydrochloric acid, and collecting the chlorine evolved in potassium iodide. Oxidation with potassium permanganate cannot be relied upon. When ammonium phosphotungstates containing  $22\text{WO}_3, \text{P}_2\text{O}_5$ , or  $24\text{WO}_3, \text{P}_2\text{O}_5$ , are dissolved in ammonia, ammonium metavanadate and then a slight excess of hydrochloric acid added, a lemon-yellow crystalline precipitate soon forms on boiling; the precipitate requires washing with dilute ammonium nitrate solution. Its composition is



A boiling solution of ammonium metavanadate dissolves the white insoluble phosphotungstate of ammonium quite readily to a very deep orange-red solution, from which in a few days deep orange or garnet-red crystals separate; they may be recrystallised from water. The salt has the composition  $16\text{WO}_3, 3\text{V}_2\text{O}_5, \text{P}_2\text{O}_5, 5(\text{NH}_4)_2\text{O} + 37\text{H}_2\text{O}$ .

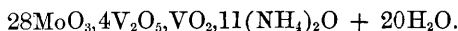
When the baric phosphotungstate (20 : 1 : 6) previously described is boiled with vanadic hydrate, an orange-red solution is formed, and on cooling octahedral crystals of a red colour separate, having the composition  $60\text{WO}_3, 3\text{P}_2\text{O}_5, 2\text{V}_2\text{O}_5, 18\text{BaO} + 144\text{H}_2\text{O}$ . The crystals dissolve rather easily in hot water, but are at the same time decomposed, with formation of other salts.

The phosphotungstate of sodium,  $24\text{WO}_3, \text{P}_2\text{O}_5, 2\text{Na}_2\text{O}, 4\text{H}_2\text{O} + 23\text{Aq}$ , is readily dissolved on boiling it with a solution of ammonic metavanadate; this solution does not deposit crystals, but on adding a large excess of potassium bromide, an orange-red crystalline precipitate forms. Its composition is expressed by the formula



Hot water dissolves, but decomposes this salt, an orange-brown crystalline salt, having the formula  $7\text{WO}_3, \text{V}_2\text{O}_5, \text{P}_2\text{O}_5, 3\text{K}_2\text{O} + 11\text{H}_2\text{O}$  being formed. The existence of other, i.e., sodium, ammonium, and trimethylammonium-vanadio-phosphotungstates is pointed out.

*Vanadio-vanadico-molybdates*.—These and other similar salts contain two oxides, viz.,  $\text{R}_2\text{O}_5$  and  $\text{R}'\text{O}_2$ , in which, however, R and R' may be identical. They are very readily formed by boiling a mixture of the two oxides of vanadium with an acid molybdate; by the partial reduction of vanadio-molybdates; or by digesting solutions of acid molybdates with solutions which contain vanadic dioxide and pentoxide. By igniting ammonium divanadate and boiling the residue with acid ammonium molybdate (viz., the salt 14 : 6), a solution is obtained, which, on evaporation, deposits pale greenish-yellow crystals; these may be recrystallised; their composition is expressed by

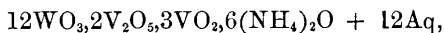


Barium chloride added to the mother-liquor of the preceding salt,



gives a pale-yellow crystalline precipitate, having the composition  $30\text{MoO}_3, 2\text{V}_2\text{O}_5, 3\text{VO}_2, 14\text{BaO} + 48\text{Aq.}$

*Vanadio-vanadico-tungstates.*—By boiling a commercial vanadic pentoxide with acid sodium tungstate (viz., the salt 12 : 5) and evaporating to a syrup, large orange-red crystals, probably having the formula  $12\text{WO}_3, 2\text{V}_2\text{O}_5, 3\text{VO}_2, 6\text{Na}_2\text{O} + 43\text{Aq.}$  are obtained. In an exactly similar manner a potassium and an ammonium salt, probably



may be obtained. These salts give with silver nitrate a scarlet crystalline precipitate,  $12\text{WO}_3, 2\text{V}_2\text{O}_5, 3\text{VO}_2, 6\text{Ag}_2\text{O} + 8\text{Aq.}$  The preparation of these salts could not be repeated, using a mixture of vanadic dioxide and pentoxide, and the analyses being incomplete, the formulæ given cannot be considered as definitely proved.

*Phospho-vanadio-vanadico-tungstates.*—These salts, which may be regarded as double salts, are formed whenever phosphotungstates are mixed with vanadates in presence of vanadic dioxide; when vanadio-vanadico-tungstates are heated with alkaline phosphates or phosphoric acid; and when phosphovanadates and alkaline tungstates are brought together in presence of a reducing agent and of an acid. They are either green or orange-red. When the residue left on heating ammoniac vanadate is added gradually to a boiling solution of barium phosphotungstate,  $2\text{WO}_3, \text{P}_2\text{O}_5, 6\text{BaO}$ , and the solution filtered and evaporated, deep green crystals are obtained, having the composition  $60\text{WO}_3, 3\text{P}_2\text{O}_5, \text{V}_2\text{O}_5, \text{VO}_2, 18\text{BaO} + 150\text{H}_2\text{O}$ . This and similar salts are oxidised by bromine or nitric acid, but not by cold potassium permanganate solution; probably the salt  $60\text{WO}_3, 3\text{P}_2\text{O}_5, \text{V}_2\text{O}_5, \text{VO}_2, 18\text{BaO} + 144\text{H}_2\text{O}$  already described is formed. In many cases these complex salts may be considered as double or triple salts, in which the individual members belong to or at least correspond with known classes of salts. The salts described belong to the four classes—

1.  $m\text{RO}_3.n\text{V}_2\text{O}_5.p\text{R}'_2\text{O}$ ;
2.  $m\text{RO}_3.n\text{P}_2\text{O}_5.p\text{V}_2\text{O}_5.v\text{H}_2\text{O}$ ;
3.  $m\text{RO}_3.n\text{P}_2\text{O}_5.p\text{V}_2\text{O}_5.r\text{VO}_2.v\text{H}_2\text{O}$ ;
4.  $m\text{RO}_3.n\text{V}_2\text{O}_5.p\text{VO}_2.v\text{H}_2\text{O}$ .

In other communications the author will show that other metals than vanadium may occupy the place of  $\text{R}'_2\text{O}$ , that other pentoxides than  $\text{P}_2\text{O}_5, \text{As}_2\text{O}_5$ , and  $\text{V}_2\text{O}_5$  may occupy the place of  $\text{R}_2\text{O}_5$  in the above formulæ, and that the complex inorganic acids form a new department of inorganic chemistry, and not a series of isolated compounds.

H. B.

**Arsenomolybdic Acid.** By O. PUFAHL (*Ber.*, 17, 217—218).—By decomposing barium molybdate suspended in an aqueous solution of arsenic acid with sulphuric acid, a yellow liquid is obtained, which on evaporation yields arsenomolybdic acid, crystallising in two forms, in groups of doubly refracting orange-red needles, and in efflorescent yellow tabular crystals (apparently monoclinic). The pure saturated aqueous solution has the sp. gr. 2.45 at 18.3°. The yellow crystals probably differ from the red merely in containing a larger amount of water of crystallisation. Analysis of the somewhat impure acids

gave for the red crystals the atomic ratios 1  $\text{As}_2\text{O}_5$  : 18.09  $\text{MoO}_3$  : 29.97  $\text{H}_2\text{O}$ , for the yellow crystals 1  $\text{As}_2\text{O}_5$  : 18.96  $\text{MoO}_3$  : 39.35  $\text{H}_2\text{O}$ . Numerous salts have been prepared, and will be described later.

A. J. G.

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## Mineralogical Chemistry.

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**Pachnolite and Thomsenolite.** By DES CLOIZEAUX (*Ann. Chim. Phys.* [5], 29, 392—400).—The crystallographic and optical examination of these two minerals, which according to Brandl differ in chemical composition (Abstr., 1883, 29), shows them to be two distinct species. In pachnolite the axes have the proportion  $c : b : a = 1.326676 : 1 : 0.859495$ .  $\beta = 89.41^\circ$ ; in thomsenolite the proportions  $c : b : a = 1.0883 : 1 : 0.998741$ .  $\beta = 89.1^\circ$ . P. P. B.

**Manganese in the Cipolin Marbles of Primary Formations.** By DIEULAFAIT (*Compt. rend.*, 98, 634—636).—The term "cipolin marble" is given to concretionary masses of limestone found in the lower parts of beds of gneiss, sometimes in large quantities, sometimes in isolated lenticular masses, and which are evidently contemporaneous with the rocks by which they are enclosed. The author has examined more than a thousand specimens of these marbles from different parts of the world, and finds that in all cases manganese can be detected in 0.5 gram of the marble, and in the majority of cases in a few centigrams.

When calcium carbonate is brought in contact with water containing an iron and manganese salt in solution, the iron is completely precipitated, but the greater part of the manganese salt remains in solution. In the case of a magma having the composition of gneiss, i.e., composed mainly of silica and alumina, and containing a notable quantity of calcium carbonate and sensible quantities of iron and manganese, water charged with carbonic acid would dissolve out the calcium carbonate and the manganese, and would leave the greater part of the iron undissolved. The calcium carbonate afterwards deposited from this solution would be white, and would retain the greater part of the manganese which had dissolved with it. This theory explains the concentration of manganese in these cipolin marbles, also how a white and approximately pure marble can be formed in presence of a complex and highly coloured substance such as gneiss, and why the cipolin marbles are generally lenticular in shape and concretionary in structure.

It follows that the cipolin marbles and the gneiss surrounding them must be contemporaneous, and must both have been formed under water. This last conclusion is supported by many other facts.

C. H. B.

**Felspar.** By BECKER (*Dingl. polyt. J.*, 251, 287).—The author states that the largest supplies of felspar come from the Norwegian

towns Moss, Christiania, Bergen, and Arendal. Swedish felspar is principally obtained from the quarries owned by the Rörstrand Company. The author gives analyses of the following specimens :—I and II, red and white Rörstrand spar ; III, grey Norwegian spar ; IV and V, light and dark Norwegian spar, examined by Aron :—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Fe <sub>2</sub> O <sub>3</sub> .
I ..	64·57	19·73	0·18	—	12·26	3·06	0·20
II ..	61·55	23·80	3·98	—	0·38	9·67	—
III ..	63·25	19·96	0·55	0·21	14·32	1·36	0·35
IV ..	65·12	18·00	—	traces	12·89	3·00	0·78
V ..	65·54	18·31	—	traces	12·53	3·17	0·74

D. B.

**Gadolinite from Ytterby.** (Part II.) By C. AUER V. WILSBACH (*Monatsh. Chem.*, 5, 1—15).—A description of spectroscopic methods and apparatus used in this research.

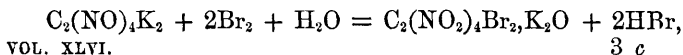
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## Organic Chemistry.

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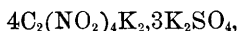
**Nitro-derivatives of Ethane.** By A. VILLIERS (*Compt. rend.*, **98**, 431—433).—The author has previously shown (*Compt. rend.*, **97**, 258) that the first product of the reducing action of ammonium hydrosulphide on the potassium compound of tetranitro-ethylene dibromide is the compound  $C_2K_2(NO_2)_4$ . Prolonged action of the same reagent produces a base which contains potassium and sulphur, and forms a platinochloride, but this base has not yet been obtained in quantity sufficient for analysis.

When the potassium compound of tetranitro-ethylene dibromide,  $C_2(NO_2)_4Br_2 \cdot K_2O$ , is treated with free sulphurous acid, it is completely reduced with formation of ammonia, hydrobromic acid, and hydrocyanic acid. If, however, it is triturated with a solution of potassium sulphite and potassium carbonate, carbonic anhydride is given off, and a sulphur-yellow compound is obtained. This compound can be recrystallised from boiling water, and forms brilliant sulphur-yellow crystals of the composition  $4C_2(NO_2)_4K_2 + 3K_2SO_4$ . It explodes at about  $210^\circ$ , and in this respect resembles the compound  $C_2(NO_2)_4K_2$ . The same substance is formed by the direct combination of potassium sulphate with the compound  $C_2(NO_2)_4K_2$  obtained by the action of ammonium hydrosulphide. Its formation by the first method takes place in accordance with the equation  $C_2(NO_2)_4Br_2 \cdot K_2O + 2K_2SO_3 + H_2O = C_2(NO_2)_4K_2 + 2K_2SO_4 + 2HBr$ , the theoretical yield being obtained. The liberation of hydrobromic acid necessitates the addition of potassium carbonate, otherwise the liquid would become acid, and total reduction would take place. The reverse reaction,



takes place readily when bromine is added to an alkaline solution of  $C_2(NO_2)_4K_2$ . A similar reaction takes place with iodine or chlorine, and from the products in these cases tetranitro-ethylene chloride or iodide can be prepared.

When a hot concentrated solution of the compound



is treated with barium chloride and filtered, the filtrate on cooling deposits brilliant pale-yellow crystals of the compound  $C_2(NO_2)_4K_2$ , which can be easily prepared in this way. C. H. B.

**Methylene Bromide.** By L. HENRY (*Ann. Chim. Phys.* [5], 30, 266—274).—Methylene bromide can be prepared without difficulty by the process indicated in outline by Butlerow, viz., by the decomposition of methylene iodide by bromine,  $CH_2I_2 + 2Br_2 = CH_2Br_2 + 2BrI$ . Thus obtained, methylene bromide is a colourless mobile liquid, of a sweet taste, boiling at  $98.5^\circ$  under a pressure of 756 mm. Its expansion may be expressed by the formula  $V = 1 + 0.001001t + 0.000001859t^2$ , hence  $\frac{dV}{dt^\circ} + \frac{V_{10}}{V_0} = 0.0009736 =$  coefficient of expansion at  $0^\circ$ ; its sp. gr. = 2.493. Methylene bromide is insoluble in water, soluble in alcohol; it does not solidify at  $-12^\circ$ . On heating it with potassium phenate, it is converted into methylene diphenylate,  $CH_2(OPh)_2$ , a colourless liquid, boiling at  $294^\circ$ ; sp. gr. = 1.1136.

A comparison of the chloro- and bromo-derivatives of methane shows that the replacement of chlorine by bromine in the molecule raises the boiling point by about  $40^\circ$ . The bromine derivatives of methane exhibit a remarkable gradation in their physical properties, as shown in the table appended:—

	Boiling point.	Specific gravity.
$CH_4$ .....	Gas	—
$CH_3Br$ .....	$4.5$	$1.732$
$CH_2Br_2$ .....	$98.5$	$2.493$
$CHBr_3$ .....	$151.2$	$2.834$
$CBr_4$ .....	$189.5$	solid

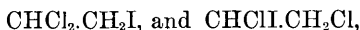
It is to be observed that the differences between two consecutive terms are not constant, but they diminish as the series progresses; this is in accordance with the observed generality. Similarly the differences in volatility and density are more marked in the successive members of the iodo-substitution series, less marked in the bromo-, and least in the chloro-series, thus:—

	Difference of boiling point.	Difference of sp. gr.
$CH_3Cl$ } .....	$65$	$0.4081$
$CH_2Cl_2$ }		
$CH_3Br$ } .....	$94$	$0.7610$
$CH_2Br_2$ }		
$CH_3I$ } .....	$137$	$1.1430$
$CH_3I_2$ }		

V. H. V.

**Action of Iodine Chloride on Monochlorethylene.** By L. HENRY (*Compt. rend.*, **98**, 518—520).—The author proposes to study the products obtained by the union of iodine monochloride with the monohaloid derivatives of ethylene, with a view to determine the behaviour of the iodine and chlorine in contact with the two chains  $\text{CHX}$  and  $\text{CH}_2$ , and the influence exerted on the reaction by the nature of the haloid X.

Monochlorethylene is slowly absorbed by an aqueous solution of iodine monochloride with formation of dichloromoniodoethane,  $\text{C}_2\text{H}_3\text{Cl}_2\text{I}$ , a colourless liquid which rapidly becomes purple on exposure to light. It has a faint ethereal odour, and a sharp, sweet taste: it boils at  $171\text{--}172^\circ$  with slight decomposition under a pressure of 774 mm.; sp. gr. at  $0^\circ = 2.2187$ . When treated with an equivalent quantity of potash in alcoholic solution, it is readily decomposed with precipitation of potassium chloride and iodide in the proportion of  $4\text{KI}$  to  $\text{KCl}$ ; with soda, a precisely similar decomposition takes place, but the sodium iodide remains in solution in the alcohol. When the alcoholic liquid is mixed with water, a heavy oily liquid separates out, and this on fractionation yields unsymmetrical dichlorethylene,  $\text{CH}_2\text{CCl}_2$ , boiling at  $35\text{--}37^\circ$ , and a much smaller quantity of unsymmetrical chloriodo-ethylene,  $\text{CH}_2\text{CCH}$ , boiling at  $101\text{--}102^\circ$  under ordinary pressure. Dichlorethylene,  $\text{CH}_2\text{CCl}_2$ , has no action on alkaline iodides even in boiling alcoholic solution, and it follows that the chloriodo-ethylene is not the product of any secondary reaction. The product of the union of monochlorethylene and iodine monochloride is a mixture of the two isomerides,



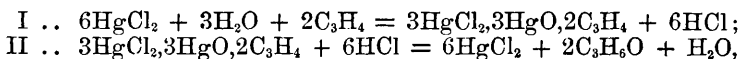
which cannot be separated by distillation because they have practically the same boiling points. It follows that the two radicles I and Cl in the system  $\text{ICl}$  combine simultaneously with each of the mono-carbon chains  $\text{CHCl}$  and  $\text{CH}_2$ , but in unequal proportion, the chlorine combining most readily with the carbon to which chlorine is already attached, whilst the less negative radicle iodine combines most readily with the most highly hydrogenised carbon in the approximate ratio of 4 to 1.

When iodine monochloride acts on monobromethylene, the distribution of iodine and chlorine in the products, with respect to the two atoms of carbon, does not follow the same law as in the case of the monochlorinated derivative.

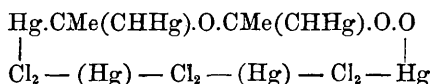
C. H. B.

**Action of the Hydrocarbons of the Acetylene Series on Mercuric Oxide and its Salts.** By M. KUTSCHEROFF (*Ber.*, **17**, 13—29).—The direct addition of the elements of water to the above hydrocarbons by the action of mercuric bromide was previously described by the author (*Abstr.*, 1881, 883), who now shows that this reaction may be brought about to a greater or less extent by all mercuric salts. On passing allylene into a solution of mercuric chloride at the ordinary temperature, a white-crystalline precipitate,  $3\text{HgCl}_2, 3\text{HgO}, 2\text{C}_3\text{H}_4$ , is obtained, whilst hydrochloric acid is liberated. The precipitate is insoluble in water and cold alcohol, but readily

soluble in hydrochloric and acetic acids with formation of a mercuric salt and acetone. The process of hydration therefore consists of two reactions—



which, according to circumstances, may take place separately or simultaneously. If the precipitate is heated along with the acid liquid, the mercuric chloride is re-formed, and may thus be employed to convert unlimited quantities of allylene into acetone. The corresponding reaction between allylene and mercuric bromide takes place to a much less extent, whilst with mercuric iodide there appears to be no action. With mercuric sulphate, allylene yields a copious white precipitate,  $\text{HgSO}_4 \cdot 5\text{HgO} \cdot 3\text{C}_3\text{H}_4 + 7\text{H}_2\text{O}$ , sparingly soluble in sulphuric, readily in hydrochloric acid, whilst with mercuric acetate it produces an amorphous precipitate,  $\text{Hg}(\text{OAc})_2 \cdot 3\text{HgO} \cdot 2\text{C}_3\text{H}_4$ , which is readily decomposed by acetic and hydrochloric acids. The author regards these complex substances as compounds of basic mercury salts, with the group  $\text{C}_3\text{H}_4\text{HgO}$  (*i.e.*, acetone in which Hg replaces  $\text{H}_2$ ), the general formula for them being  $n\text{HgX}_2 \cdot p\text{HgO} \cdot q(\text{C}_3\text{H}_4\text{HgO})$ , but attempts to separate the compound  $\text{C}_3\text{H}_4\text{HgO}$  by the action of alkali were without success. The formula,



obtained from mercuric chloride indicates the way in which the elements may be assumed to be grouped.

By the action of ethylacetylene on mercuric chloride, the compound  $3\text{HgCl}_2 \cdot \text{HgO} \cdot \text{C}_4\text{H}_6\text{HgO}$ , is obtained, and is perfectly analogous to the corresponding allylene compound; it dissolves readily in hydrochloric acid, yielding methyl ethyl ketone. When mercuric oxide, suspended in a large quantity of water, is agitated for several days with allylene, the gas is absorbed whilst the colour of the oxide changes to a dirty olive-green; on filtering and extracting with hot alcohol, a crystalline substance,  $\text{Hg}(\text{C}_3\text{H}_3)_2$ , may be obtained. It has a characteristic garlic odour, is insoluble in water, and almost insoluble in cold alcohol, whilst hydrochloric and acetic acids dissolve it with evolution of allylene. In alcoholic solution, it yields a white crystalline precipitate with mercuric chloride; this is insoluble in water and alcohol, but soluble in acids with production of acetone. The compound  $\text{Hg}(\text{C}_3\text{H}_3)_2$  can also be obtained by the action of allylene on an alkaline solution of mercuric iodide in potassium iodide, or on an alkaline solution of mercuric chloride.

A. K. M.

**Formation of Mannitol from Dextrose and Lævulose.** By F. W. DAFERT (*Ber.*, 17, 227—228).—The products of the oxidation of mannitol vary according to the nature of the oxidising agent, the temperature and the duration of oxidation; there have been observed carbonic anhydride, water, formic acid, mannitic acid, saccharic acid, inactive tartaric acid and probably glycollic acid; there are also in-



variably obtained by careful working a mannitan-like substance and mannitose. Mannitose is decidedly a glucose, it differs from dextrose in its behaviour with hydrochloric acid, sulphuric acid, Fehling's and Knapp's solutions, and in its optical inactivity. It shows the closest similarity with lævulose in all but its optical properties.

A. J. G.

**Inversion of Cane-sugar by Acids.** By F. URECH (*Bied. Centr.*, 1883, 501).—It is proved that when sugar is mixed with dilute acids, inversion goes on gradually in the cold. The relation between this reaction, which is always accompanied by development of heat, and time, and mass, and temperature, has now been investigated. The author watched the progress of inversion either in the polariscope, while the change was taking place, or by intermittent testings with Fehling's solution.

D. A. L.

**Action of Dilute Hydrochloric Acid on Starch.** By F. ALLIHN (*Dingl. polyt. J.*, 250, 554).—The subjoined table gives the results of the author's experiments on the saccharification of starch by means of dilute hydrochloric acid. The starch used contained 98·6 per cent. of pure starch, 0·9 per cent. ash, and 0·3 per cent. insoluble residue:

Duration of experiment.	Proportion of hydrochloric acid used.				
	10 p. c.	5 p. c.	3·5 p. c.	2 p. c.	1·33 p. c.
	Proportion of starch saccharified.				
Minutes.	p. c.	p. c.	p. c.	p. c.	p. c.
2	92·6	—	—	—	—
5	92·1	—	—	—	—
10	—	90·6	—	—	—
15	91·7	—	—	—	—
30	89·6	94·3	93·27	89·94	—
50	87·4	93·3	—	—	—
60	—	—	94·65	93·68	87·85
90	—	—	94·49	95·05	92·87
105	—	—	—	94·89	—
120	—	—	—	—	93·84
150	—	—	—	—	94·65

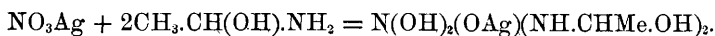
Although it would not be practicable to use hydrochloric acid on a large scale for the saccharification of starch owing to the cost of its subsequent removal, its use is recommended for laboratory purposes, *e.g.*, for the preparation of grape-sugar from starch.

D. B.

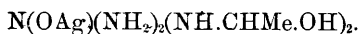
**Argentammonium Compounds.** By A. REYCHLER (*Ber.*, 17, 41—48).—When aldehyde is added to an aqueous solution of silver nitrate (1 mol.) and ammonia (1 mol.), a crystalline precipitate is obtained of varying composition; a similar result is obtained if

diammonio-silver nitrate be employed. To obtain a pure product, 100 c.c. silver nitrate solution ( $\frac{3}{8}$  normal) are mixed with 15 c.c. ammonia solution (4 times normal), the precipitated silver oxide separated, and then aldehyde added until the precipitate produced does not readily dissolve on shaking; a second quantity (15 c.c.) of ammonia solution is now added, when six-sided scales separate. The product,  $C_4H_{10}N_3O_3Ag \cdot \frac{1}{2}H_2O$ , is sparingly soluble in water, less so in alcohol, and almost insoluble in ether, the aqueous solution yielding a silver mirror when warmed. It is gradually decomposed at  $100^\circ$ , melts somewhat higher and detonates. By the action of dry ammonia on the powdered substance, 2 mols. of the gas are absorbed with development of heat, the product containing 1 atom of silver to 4 atoms of ammoniacal nitrogen. To prepare the anhydrous compound  $C_4H_{10}N_3O_3Ag$ , a dilute alcoholic solution of aldehyde (20 c.c.) and ammonia (6—8 mols.) is precipitated with silver nitrate solution (1 mol.), when it is obtained in crystalline grains or scales. This compound also absorbs dry ammonia with formation of a product containing 4 atoms of ammoniacal nitrogen to 1 atom silver.

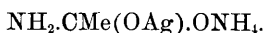
In explanation of the action of silver nitrate on aldehyde-ammonia, the author suggests the following equation:—



By the abstraction of 2 mols.  $H_2O$  from the product, the anhydrous compound  $C_4H_{10}N_3O_3Ag$  is produced, the constitution of which may be expressed thus:  $N(OAg)(\overset{O}{\underset{NH}{>}}CHMe)_2$ , and that of the compound obtained by the addition of ammonia is—



Diammonio-silver acetate,  $C_2H_3O_2Ag \cdot 2NH_3$ , is obtained by passing dry ammonia over silver acetate. The product is a white substance which loses ammonia on exposure to air, and dissolves readily in water. Its constitution may be expressed thus:



On adding aldehyde to an aqueous solution of diammonio-silver acetate, a crystalline precipitate is obtained, consisting, however, of impure silver acetate; a compound of silver acetate with ammonia and aldehyde could not be obtained.

A. K. M.

**Action of Acetic Anhydride on Amidines.** By A. PINNER (*Ber.*, 17, 171—178).—The author has already shown (*Abstr.*, 1883, 1099) that acetic anhydride acts differently on various amidines; the present paper gives further studies on the subject. All the experiments were conducted in the same manner: the amidine hydrochloride was mixed with an equivalent quantity of freshly fused sodium acetate, so much acetic anhydride being added that the mixture formed a thick pulp, which was then heated to gentle boiling for 1—2 hours in a vessel provided with a reflux condenser.

From formamidine there was obtained diacetylformamidine,



(*loc. cit.*) and *triacetylformamidil*,  $C_8H_{11}N_3O_3$ . The latter crystallises in hard crusts formed of prisms, melts at  $224^\circ$ , is very sparingly soluble in cold water, more readily in hot water. It must be regarded as the triacetyl-derivative of the condensation product  $C_2H_5N_3$ , whose constitution is as yet uncertain. On boiling diacetylformamidine with water, it is decomposed with formation of acetamide; acetamide is also formed on heating it at  $150^\circ$ .

The product of the reaction of acetic anhydride on acetamidine was poured into aqueous soda, and the crystalline mass which separated recrystallised. It consisted of two substances, of which that soluble in water, *anhydrodiacetylacetamidil*,  $C_8H_{11}N_3O$ , crystallises with 2 mols. of water in groups of minute prisms, loses its water of crystallisation over sulphuric acid, volatilises slowly at  $100^\circ$ , and melts at  $185^\circ$ . It is readily soluble in alcohol and dilute acids, has marked basic properties, and yields a readily soluble platinochloride decomposing on fusion. The substance, insoluble in water, *anhydrodiacetylacetamidine*,  $C_6H_8N_2O$ , crystallises in lustrous needles, melts at  $253^\circ$  to a dark-coloured liquid, is sparingly soluble in cold, readily soluble in hot alcohol, very soluble in dilute acids. The platinochloride crystallises in yellow needles very soluble in water.

Capronamidine when treated in the manner described above yields capronitrile.

Further researches are necessary to ascertain the constitution of the new substances described.

**AMIDINE SALTS.** *Acetamidine hydrochloride* crystallises in long, brilliant, transparent prisms, is somewhat deliquescent, and melts at  $164$ – $165^\circ$ . *Acetamidine platinochloride*,  $(CMeN_2H_3)_2H_2PtCl_6$ , forms moderately soluble, yellowish-red prisms; on boiling it with water, ammonium platinochloride separates.

*Propionamidine hydrochloride*,  $C_3H_7N_2.HCl$ , forms deliquescent, long, broad needles, melts at  $129^\circ$ , is readily soluble in alcohol, insoluble in ether. The *platinochloride*,  $(C_3H_7N_2)_2H_2PtCl_6$ , forms yellowish-red crystals, rather sparingly soluble in water; it melts with slow decomposition at  $199$ – $200^\circ$ .

*Capronamidine hydrochloride*,  $C_6H_{14}N_2.HCl$ , forms large plates, melts at  $106$ – $107^\circ$ , is somewhat deliquescent, and is readily soluble in alcohol. The *platinochloride*,  $(C_6H_{14}N_2)_2H_2PtCl_6$ , forms yellowish-red plates, sparingly soluble in cold, readily soluble in hot water; it melts under hot water, but when dry melts with decomposition at  $199^\circ$ .

*Capronimido-ether hydrochloride* solidifies when cooled below  $0^\circ$ , and melts on heating to the ordinary temperature; when carefully decomposed with soda, it yields *capronimido-ether*,  $C_5H_{11}.X(OEt):NH$ , as a liquid of peculiar odour boiling at  $168^\circ$ , and but little soluble in water.

A. J. G.

**Action of Heat on Amidine Hydrochlorides.** By A. PINNER (*Ber.*, 17, 179–182).—The author has shown (Abstr., 1883, 1090) that by heating ethylamine with a formimido-ether hydrochloride he obtained, not diethylformamidine hydrochloride as expected, but the salt of a base,  $C_{10}H_{21}N_3$ , derived from diethylformamidine by elimination of ammonia. The non-occurrence of diethylformamidine is now

found to be due to its decomposition by the temperature employed in the reaction. A mixture of diethylamine and formimido-ether hydrochloride dissolved in absolute alcohol was allowed to remain for several weeks at the ordinary temperature; the products of the reaction were then found to be ammonia, diethylamine hydrochloride, diethylformamidine hydrochloride, and the hydrochloride of the base  $C_{10}H_{21}N_3$ .

*Unsymmetrical diethylformamidine hydrochloride*,  $NEt_2 \cdot CH:NH \cdot HCl$ , crystallises in brilliant, transparent, compact prisms, melts at  $125^\circ$ , is very hygroscopic, and is readily soluble in alcohol. The platinochloride,  $(C_5H_{12}N_2)_2 \cdot H_2PtCl_6$ , crystallises in yellowish-red prisms, melts at  $208-209^\circ$ , and is sparingly soluble in cold water. When the alcoholic solution of the hydrochloride is boiled it slowly evolves ammonia. Formamidine hydrochloride evolves streams of ammonia when heated in alcoholic solution.

A. J. G.

**Glucosamine Hydrochloride.** By F. TIEMANN (*Ber.*, **17**, 241—251).—G. Ledderhose gave the name glucosamine hydrochloride to a crystalline substance,  $C_6H_{13}NO_5 \cdot HCl$ , obtained by boiling chitin with concentrated hydrochloric acid. By double decomposition with silver salts, he obtained what he regarded as salts of glucosamine, and free glucosamine by treatment of the sulphate with barium hydroxide, all these substances being distinctly crystalline, but none of these derivatives from the hydrochloride could be obtained in a state fit for analysis. Moreover, on heating glucosamine hydrochloride with a nitrite, nitrogen was evolved, and he obtained a sugar (of the formula  $C_6H_{12}O_6$ ?) as a dextrorotary syrup (this *Journal*, 1877, **1**, 64; *Zeitschr. Physiol. Chem.*, **2**, 213; **4**, 139).

To prepare glucosamine hydrochloride, the claws and shells of lobsters were treated at the ordinary temperature with concentrated hydrochloric acid until all mineral matters had been removed, and then dissolved in boiling hydrochloric acid. The solution was diluted with water, the excess of acid evaporated, filtered after some time to remove separated black decomposition-products, and finally crystallised. The last crystallisations are especially liable to contain gypsum, the presence of which leads to erroneous conclusions as to the crystallisation of the derivatives. Attempts to prepare the sulphate, nitrate, &c., and the free base were not more satisfactory than those of Ledderhose; syrups were obtained which only crystallised in part after standing for more than a year under absolute alcohol. There seems great doubt if some further decomposition had not occurred during these attempts to prepare the salts and the base, inasmuch as it was not found possible to reconvert these crystalline products into glucosamine hydrochloride. The author confirms Ledderhose's statement as to the action of nitrites on glucosamine hydrochloride, and was also unable to obtain the sugar in a state fit for analysis.

By careful oxidation of glucosamine hydrochloride with nitric acid, (sp. gr. 1.2) isosaccharic acid is obtained. If the reaction is allowed to become violent, oxalic acid is formed in large quantity, but with care its formation can be almost entirely avoided.

*Isosaccharic acid*,  $C_6H_{10}O_8$ , crystallises in anhydrous white rhombic crystals, melts at  $185^\circ$ , and is decomposed on stronger heating. It is readily soluble in alcohol and water, more sparingly soluble in ether. Its aqueous solution is dextrorotary. The barium salt,  $C_6H_8BaO_8$ , forms crystalline crusts; the copper salt,  $C_6H_8CuO_8$ , is obtained as a light green crystalline precipitate on adding alcohol to its aqueous solution; the calcium salt,  $C_6H_8CaO_8$ , forms pointed crystals. The silver salt,  $C_6H_8Ag_2O_8$ , is obtained as a white crystalline precipitate on adding silver nitrate to a concentrated solution of the calcium salt; on boiling its aqueous solution silver separates, in part as a mirror.

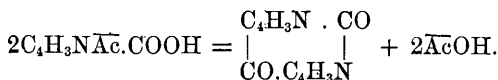
*Ethyl isosaccharate*,  $C_6H_8O_6(OEt)_2$ , crystallises in concentrically grouped needles, melts at  $73^\circ$ , is readily soluble in water, alcohol, and ether, sparingly soluble in chloroform and benzene. By carefully heating isosaccharic acid in a stream of carbonic anhydride nothing but a small carbonaceous residue is left, the acid being almost entirely resolved into carbonic anhydride, water, and pyromucic acid.

A careful comparison of isosaccharic acid with the isomeric saccharic, mucic, and paramucic acids, clearly showed that it was not identical with any of them.

**New Group of Nitrogen Compounds.** By R. ENGEL (*Compt. rend.*, **98**, 574—576).—When ammonium lactate is dried in a slow current of dry ammonia gas and heated above  $160^\circ$ , it is completely decomposed; at  $125$ — $135^\circ$  it gradually gives off water, and is mainly converted into lactamide; at  $95$ — $105^\circ$  it loses water very slowly, but after 456 hours' heating the residue has the same composition as lactamide. The product, however, differs in its properties from both lactamide and alanine. It is a pale amber-coloured, syrupy uncrystallisable liquid, which decomposes at about  $200^\circ$ , and cannot be distilled. In contact with water, it immediately forms ammonium lactate, and the whole of the ammonia contained in it can be precipitated by platinum chloride in the cold. The constitution of this new compound may be represented by the formula  $CHMe < \begin{smallmatrix} NH_3 \\ CO- \end{smallmatrix} > O$ , it being formed from ammonium lactate by the loss of the alcoholic hydroxyl and one of the hydrogen-atoms in the ammonium. This formula explains the readiness with which the compound is converted into ammonium lactate, and also shows that it is intermediate between an ammonium salt and an amine. Hence the author proposes to call this new isomeride *lactamine*, and to give the generic name *acidamines* to other compounds of the same nature, which will be described in a subsequent paper. C. H. B.

**Synthesis of Pyrocoll.** By G. L. CIAMICIAN and P. SILBER (*Ber.*, **17**, 103—106).—This is effected by means of the acetyl-derivative of carbopyrrollic acid. The authors prepare carbopyrrollic acid by Schwanert's method (*Annalen*, **116**, 278) of heating ammonium mucate, and saponifying the carbopyrrolamide obtained with baryta-water. They then convert the barium salt into potassium or sodium salt, add dilute sulphuric acid, and extract with ether. To prepare

pyrocoll, carbopyrrollic acid is boiled with an excess of acetic anhydride, and the latter then removed by distillation under diminished pressure. When the nearly black and thick oil obtained is further heated at about 160—190°, acetopyrroline passes over with the last traces of acetic anhydride; at a certain stage, however, the residue suddenly boils up with abundant evolution of acetic acid, and solidifies. The heating is then discontinued, and the product purified by crystallisation from glacial acetic acid and sublimation in a current of carbonic anhydride. Its properties agree with those of pyrocoll obtained from gelatin; it melts at 267°. The authors have not been able to isolate the acetyl-derivative of carbopyrrollic acid, which appears to be decomposed by boiling with water. The production of pyrocoll may be explained by the equation:—



A. K. M.

**Influence of Isomerism on Etherification.** By N. MENSCHUTKIN (*Ann. Phys. Chim.* [5], 30, 81—144).—The greater part of the results and the deductions therefrom brought forward in this memoir have already appeared in abstract (*Abstr.*, 1882, 383—388).

Some few miscellaneous experiments are added, together with general conclusions from the whole of the author's researches.

*Etherification of Halogen-derivatives of Alcohols by Acetic Acid.*

	Initial velocity.	Limit.
Glycol chlorhydrin, $\text{CH}_2\text{Cl}.\text{CH}_2.\text{OH}$ . . . . .	48·86	—
Glycerol dibromhydrin, $\text{CH}_2\text{Br}.\text{CHBr}.\text{CH}_2.\text{OH}$ . . . . .	15·51	—

*Etherification of Derivatives of Acids by Isobutyl Alcohol.*

	Initial velocity.	Limit.
Monochloracetic acid, $\text{CH}_2\text{Cl}.\text{COOH}$ . . . . .	64·42	—
Metanitrobenzoic acid, $\text{C}_6\text{H}_4\text{NO}_2.\text{COOH}$ . . . . .	24·76	72·28

*Etherification of Various Alcohols by Acetic Acid.*

	Initial velocity.	Limit.
Propargylic alcohol, $\text{CH}:\text{C}.\text{CH}_2.\text{OH}$ . . . . .	20·50	—
Ethyl isobutyl carbinol, $\text{CHMe}_2.\text{CH}_2.\text{C}^t\text{H}.\text{OH}$ . . . . .	18·23	63·06
Menthol, $\text{C}_{10}\text{H}_{20}\text{O}$ . . . . .	15·29	61·49
Borneol, $\text{C}_{10}\text{H}_{18}\text{O}$ . . . . .	25·12	62·46
Ethyl phenyl carbinol, $\text{CH}^t\text{EtPh}.\text{OH}$ . . . . .	18·89	—
Diphenyl carbinol, $\text{CHPh}_2.\text{OH}$ . . . . .	21·99	—

*Conclusions.*—The principal results of the author's investigations on the influence of isomerism of alcohols and acids on the formation of ethereal salts may be summed up as follows:—

*Monatomic Alcohols.*—(i.) The primary alcohols possess the highest limit of etherification and the greatest initial velocity, but these

values are different for different isologous series, the less saturated giving results lower than the most saturated. In the homologous series of these last, the velocity and limit vary regularly with the molecular weight.

(ii.) The initial velocity and limit of the secondary is less than that of the primary alcohols; analogous differences of composition correspond with analogous differences of etherification.

(iii.) The velocity and limit of the tertiary alcohols is very small, their salts of acetic acid are readily decomposed into the acid and the corresponding olefine.

(iv.) The phenols resemble the tertiary alcohols, although the process of etherification proceeds normally.

*Polyatomic Alcohols.*—(i.) The velocity and limit of polyatomic alcohols vary inversely as their atomicity.

(ii.) With alcohols of the same atomicity, the velocity and limit vary with their isomerism; the primary glycols give the highest results, then the secondary, and the tertiary the lowest. The diatomic phenols resemble the tertiary glycols.

*Monobasic Acids.*—(i.) The etherification of the primary monobasic acids is distinguished from that of all other acids by the high initial velocity and small limit. In the homologous series of normal primary acids, the limit and velocity vary regularly with the molecular weight of the acid.

(ii.) The secondary acids show smaller initial velocities, but higher limits than the primary acids; the effect of variation of composition is not marked.

(iii.) The tertiary monobasic acids, whether of the paraffinoid or aromatic series, are characterised by the smallest velocity, but by the highest limit of etherification.

*Polybasic Acids.*—The limit of the polybasic acids is approximately equal to those of the monobasic; their initial velocity is, however, slightly greater. The influence of isomerism in both series exhibits the same characteristics.

*Hydroxyl Acids.*—(i.) The primary alcoholic acids show the highest limit of the etherification, on the action upon them of acids and alcohols, and in the process of internal etherification, or formation of anhydride.

(ii.) The phenolic acids belonging to the group of tertiary acids are characterised by the small limit in the action upon them of acids and alcohols; they do not undergo the change of internal etherification.

V. H. V.

**Ethylic Ethylacetocyanacetate and Methylacetocyanacetate.** By A. HELD (*Compt. rend.*, **98**, 522—525).—When the sodium derivative of ethylic acetocyanacetate is heated with methyl or ethyl iodide, no substitution takes place. Ethylic ethylacetocyanacetate can, however, be obtained by treating ethylic ethylacetocyanacetate with sodium ethylate, and saturating the liquid with dry cyanogen chloride. On adding water, the product separates into two layers, the upper of which is washed with water and fractionated in a vacuum. Ethylic ethylacetocyanacetate is a colourless liquid, which gradually becomes yellowish. It has an agreeable ethereal odour, boils at 105—110°

under a pressure of 15 mm. to 2 mm. of mercury, and dissolves in all proportions in alcohol and ether, but is insoluble in water and in alkaline solutions; sp. gr. at  $20^{\circ} = 0.976$ . When boiled for several hours with potash solution, it yields ammonia, carbonic anhydride, alcohol, and acetic and butyric acids, and therefore has the constitution  $\text{Me.CO.CEtCy.COOEt}$ .

Ethyl methylacetocyanacetate is prepared in a similar manner. It is a colourless liquid, which boils at  $90\text{--}95^{\circ}$  under a pressure of 15—20 mm.; sp. gr. at  $20^{\circ} = 0.996$ . It has an ethereal odour, and is insoluble in water and alkalis. When boiled with potash, it splits up in the same manner as the preceding compound, but yields propionic acid in place of butyric acid, and it therefore has the constitution  $\text{Me.CO.CMeCy.COOEt}$ .  
C. H. B.

**Reactions of Carbon Oxysulphide.** By BERTHELOT (*Ann. Chim. Phys.* [5], **30**, 539—541).—Carbon oxysulphide and ammonia gases combine to form ammonium oxysulphocarbamate transformable into carbamide by elimination of hydrogen sulphide, thus:  $\text{NH}_2.\text{COSNH}_4 - \text{H}_2\text{S} = \text{NH}_2.\text{CO.NH}_2$ . On evaporating an aqueous solution of the salt, a crystalline mass is obtained, consisting principally of carbamide admixed with a considerable proportion of thio-carbamide. The formation of this latter may be due either to simultaneous production of two isomeric oxysulphocarbamates in the reaction of ammonia on carbon oxysulphide, such as  $\text{NH}_2.\text{CO.SNH}_4$  or  $\text{NH}_2.\text{CS.ONH}_4$ , or to the concomitant elimination of hydrogen sulphide, or water from one oxysulphocarbamate.  
V. H. V.

**Malonic Acid.** By M. FREUND (*Ber.*, **17**, 133—138).—For the preparation of malonamide, the author recommends that malonic ether (50 grams) be treated with (150 c.c. of) concentrated ammonia solution (sp. gr. 0.925), and repeatedly shaken for 1—2 days. On heating an aqueous solution of the amide with freshly precipitated mercuric oxide, the compound  $\text{CH}_2\langle\begin{smallmatrix} \text{CONH} \\ \text{CONH} \end{smallmatrix}\rangle\text{Hg}$  is produced, and separates on cooling as a heavy white amorphous powder, insoluble in alcohol and ether, sparingly soluble in hot water, readily in dilute hydrochloric acid. *Dimethylmalonamide*,  $\text{CH}_2(\text{CO.NHMe})_2$ , is prepared by agitating malonic ether (1 mol.) with aqueous methylamine (2 mols.), and evaporating the solution to dryness. It crystallises from benzene in small flat deliquescent needles, melting at  $128^{\circ}$ . *Malonanilide*,  $\text{CH}_2(\text{CO.NHPh})_2$ , obtained by boiling malonic ether (1 mol.) with aniline (2 mols.), crystallises from alcohol in white needles melting at  $223^{\circ}$ . It can also be prepared by boiling malonamide with aniline. It is not acted on by acetic chloride, even on heating. When malonamide (1 mol.) is heated with aniline (1 mol.) in an oil-bath, the temperature being gradually raised to  $200\text{--}220^{\circ}$ , and maintained at that for about half an hour, the product solidifies on cooling; the mass is powdered, boiled with water, and the solution filtered hot. The *monophenylmalonamide*,  $\text{NH}_2.\text{CO.CH}_2.\text{CO.NHPh}$ , thus obtained, crystallises from water or alcohol in slender white needles melting at  $163^{\circ}$ . When this is boiled with an excess of milk of lime, the calcium salt



of malonanilic acid,  $(\text{NHPh}.\text{CO}.\text{CH}_2.\text{COO})_2\text{Ca}.\frac{4}{3}\text{H}_2\text{O}$ , is formed, crystallising in tufts of needles. The free acid,  $\text{C}_9\text{H}_9\text{NO}_3$ , forms large well-formed crystals melting at  $132^\circ$ . The silver salt,  $\text{C}_9\text{H}_8\text{NO}_3\text{Ag}$ , crystallises in small white needles. *Dimethyldiphenylmalonamide*,  $\text{CH}_2(\text{CO}.\text{NMePh})_2$ , is prepared by boiling malonamide with an excess of methylaniline; it crystallises from water in rhombic plates and from ether in prisms melting at  $109^\circ$ . *Ethylenemalonamide*,



is formed when ethylenediamine is heated at  $170$ – $180^\circ$  with malonamide or boiled with ethyl malonate; it is very readily soluble in water, almost insoluble in alcohol. Phenylenediamine reacts in a similar way, yielding an amorphous grey substance, insoluble in water, alcohol, ether, glacial acetic acid, and benzene. A. K. M.

**Derivatives of Malonic Acid.** By L. RÜGHEIMER (*Ber.*, 17, 235–236).—By heating equal molecular weights of aniline and ethyl malonate in sealed tubes at  $160$ – $170^\circ$ , the author obtained, not the desired malonanilic acid, but, the dianilide of malonic acid, a substance crystallising in needles melting at  $222$ – $223^\circ$ , soluble in alcohol and dilute acetic acid, insoluble in water and ether. Boiling acetic anhydride attacks this substance, converting it into a body which crystallises from light petroleum in broad needles. Treated with sulphuric acid at  $150^\circ$ , the dianilide yields an acid crystallising in large tables of the formula  $\text{C}_{15}\text{H}_{12}\text{N}_2(\text{SO}_3\text{H})_2 + 2\text{H}_2\text{O}$  (?).

*Malonanilic acid* appears to be formed by heating equal molecular weights of aniline and malonic acid at  $105^\circ$ . It crystallises in small prisms, melts with decomposition at  $132^\circ$ , and is much less soluble in water than malonic acid.

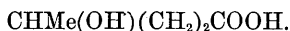
Aniline and ethyl malonylchloride,  $\text{ClCO}.\text{CH}_2.\text{COOEt}$ , dissolved in benzene, react at ordinary temperatures and yield aniline hydrochloride and a substance crystallising in needles melting at  $208$ – $210^\circ$ , but not resolidifying after fusion, soluble in aqueous ammonia and soda, sparingly soluble in sodium carbonate. A. J. G.

**Formulae of certain Ammonium Salts.** By R. ENGEL (*Compt. rend.*, 98, 628–630).—It is well known that aldehydes have a tendency to unite with water, forming hydrates which are really bivalent alcohols, the ethers of which are the acetals, and hence the existence might be inferred of a hydrate of glyoxalic acid,  $\text{COH}.\text{COOH}$ , which would be dihydroxyacetic acid,  $\text{CH}(\text{OH})_2.\text{COOH}$ . Notwithstanding the fact that glyoxalic acid and the glyoxalates contain a molecule of water which cannot be driven off without decomposing the compound, the formula  $\text{COH}.\text{COOH}$  is generally given to metallic glyoxalates, although the only fact which really supports this view is the composition of the ammonium glyoxalate,  $\text{COH}.\text{COONH}_4$ , which is regarded as a true ammonium salt, because it gives off ammonia when treated with potash, and undergoes double decomposition with other salts. The author, however, regards this compound, the corresponding ammonium mesoxalate, which contains 1 mol.  $\text{H}_2\text{O}$  less than other

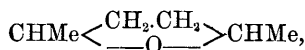
mesoxalates, and aldehyde-ammonium sulphites, which also contain 1 mol.  $\text{H}_2\text{O}$  less than the corresponding salts of other metals, as analogous to the lactamine described in a preceding communication. He regards ordinary ammonium glyoxalate and mesoxalate as glyoxal-amine and mesoxalamine respectively, and concludes: (1) that the glyoxalates have the general formula  $\text{CH}(\text{OH})_2\text{COOM}$ ; and (2) that to the acid alcohols of the formula  $\text{CH}(\text{OH})\text{COOH}$ , there corresponds a series of nitrogen compounds which are not ammoniacal salts, because they contain an atom of water less, and are not amides because they behave like ammonium salts when brought in contact with water, but which occupy an intermediate position.

C. H. B.

**Distinct Types of Glycollic Oxides.** By L. HENRY (*Ann. Chim. Phys.* [5], 29, 543—555).—It is here proposed to divide the substituted derivatives of the paraffins into two distinct types, 1st, the continuous, in which the replacing groups are attached to contiguous carbon-atoms, and 2nd, the discontinuous, in which these groups are attached to carbon-atoms, which are not contiguous. To the first class belong, for example, ordinary lactic acid,  $\text{COOH}\cdot\text{CHMe}\cdot\text{OH}$ , or propylene glycol,  $\text{CH}_2(\text{OH})\cdot\text{CHMe}\cdot\text{OH}$ ; to the second class belong  $\gamma$ -oxybutyric acid,  $\text{CH}_2(\text{OH})(\text{CH}_2)_2\text{COOH}$ , or  $\gamma$ -oxyvaleric acid,



It would appear generally that a discontinuous compound functions as a series of distinct mono-carbon groupings detached from one another, but in the continuous compounds the proximity of the substituted groupings modifies its character. Such differences of chemical function are here illustrated in the case of two glycollic oxides derivable from hexylene, the one diallyl oxide,



the other mannitic oxide,  $\text{CHMe} \searrow \text{O} \swarrow \text{CH}\cdot\text{CH}_2\text{Et}$ . The former resembles ethyl oxide in dissolving in the halogen or sulphuric acids without chemical change or evolution of heat, and in being for the most part unaltered by phosphorus pentachloride. It is immediately oxidised by nitric acid. On the contrary, the latter resembles ethylenic oxide in combining directly with the halogen acids with considerable evolution of heat, and formation of a hydride,  $\text{C}_6\text{H}_{12}\cdot\text{OH}$ ; by phosphorus pentachloride, it is converted into a dichlorhexane,  $\text{C}_6\text{H}_{12}\text{Cl}_2$ ; by nitric acid, it is converted into a binitrate,  $\text{C}_6\text{H}_{12}(\text{NO}_3)_3$ . These facts illustrate the dynamical differences between two compounds, in both of which the relative arrangement of the carbon-atoms is the same, though the position of the oxygen-atom relative to the carbon-atoms is different.

V. H. V.

**Gluconic Acid.** Preliminary Notice. By H. KILIANI and S. KLEEMANN (*Ber.*, 17, 143).—Gluconic acid is converted into caprolactone by heating it with concentrated hydriodic acid and amorphous phosphorus in a vessel provided with a reflux condenser; caproic

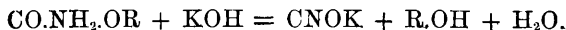
acid does not appear to be formed simultaneously. By heating caprolactone with the same reagents in sealed tubes at  $200^{\circ}$ , caproic acid is obtained. A. J. G.

**Action of Alkalis on Mucobromic Acid.** By H. B. HILL (*Ber.*, 17, 238—239).—The action of excess of baryta on mucobromic acid resolves it into formic and dibromacrylic acids (Hill and Jackson, *Abstr.*, 1879, 224); if, however, any large excess of baryta is avoided, the reaction takes quite a different course. Mucobromic acid is suspended in water, neutralised with baryta, and baryta-water slowly added, until there is  $1\frac{1}{2}$  mol. of baryta to 1 mol. of mucobromic acid, the alkaline liquid is allowed to stand all night, the excess of baryta removed with carbonic anhydride, and the filtered liquid mixed with an equal volume of alcohol, when the barium salt of an acid,  $C_6H_3BrO_4$ , is precipitated. The free acid crystallises in small colourless oblique prisms, melts at  $111$ — $112^{\circ}$ , is very soluble in water, alcohol, and ether, insoluble in chloroform, benzene, carbon bisulphide, or light petroleum. Its solutions decompose on evaporation, even at ordinary temperatures. It gives an intense garnet-red coloration with ferric chloride. The barium salt,  $BaC_4HBrO_4 + H_2O$ , crystallises in fine interlaced needles; the potassium salt,  $K_2C_4HBrO_4 + H_2O$ , crystallises in well formed rhombic tables; the silver salt,  $Ag_2HC_4BrO_4$ , is obtained as a crystalline precipitate readily soluble in nitric acid, the solution soon becoming turbid from deposition of silver bromide.

Aqueous solution of potassium phenylate reacts readily with mucobromic acid, forming *phenoxy-mucobromic acid*,  $C_6H_5(OPh)BrO_3$ .

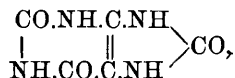
A. J. G.

**Decomposition of Ethyl Carbamate.** By G. ARTH (*Compt. rend.*, 98, 521—522).—Haller has shown that when campholurethane is treated with alcoholic potash, it splits up into potassium cyanate, borneol, and water (*Abstr.*, 1883, 625 and 1213), and the author has found that the analogous compound obtained from menthol behaves in a precisely similar manner. He now finds that when crystallised ethyl carbamate, obtained by the action of urea nitrate on absolute alcohol, is boiled with the requisite quantity of alcoholic potash, it yields potassium cyanate, which is partially decomposed with evolution of ammonia. It appears therefore that the reaction observed by Haller is general, and that when carbamic ethers are treated with potash they decompose in accordance with the equation

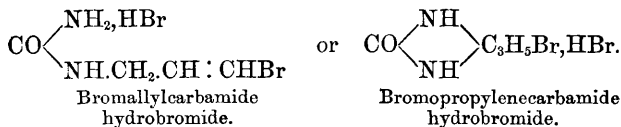


This observation furnishes an additional reason for placing the borneol and menthol derivatives referred to in the class of carbamic ethers. C. H. B.

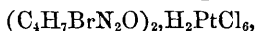
**Allylcarbamide.** (Part I.) By R. ANDREASCH (*Monatsh. Chem.*, 5, 33—46).—Looking upon Medicus' formula for uric acid,



as probably correct, the author considers that for any synthesis of uric acid which shall be of use from a theoretical point of view, the starting point must be a carbamide derivative consisting of a closed ring containing three consecutive carbon-atoms. The present investigation was undertaken in the hope of obtaining such a body by splitting off the elements of hydrobromic acid from the dibrom-addition product of allylcarbamide. Allylcarbamide was prepared by the action of allylamine sulphate on potassium cyanate, and also by heating a solution of thiosinamine with silver nitrate. Allylamine was prepared by Hofmann's method of heating allylthiocarbimide (volatile oil of mustard) with strong sulphuric acid. *Allylamine sulphate*,  $(C_3H_5.NH_2)_2.H_2SO_4$ , is very soluble in water; its solution on evaporation forms a syrup which when left for some time over sulphuric acid solidifies to a crystalline mass. It is very soluble in alcohol, and exceedingly hygroscopic. *Allylcarbamide* forms a network of fine needles easily soluble in alcohol and water, very sparingly in chloroform and ether, and melting at  $85^\circ$ . *Allylcarbamide nitrate* crystallises in groups of slender needles; it is easily soluble in water to an acid solution which decomposes with evolution of gas when heated. When an aqueous or alcoholic solution of allyl carbamide is treated with bromine, it takes up 1 mol. of the latter, forming *dibromopropylcarbamide*,  $C_4H_8N_2O.Br_2$ . The reaction takes place quantitatively, and may be used as a means of titrating a solution of allylcarbamide. Dibromopropylcarbamide crystallises in thin plates or needles, easily soluble in warm water and in alcohol, sparingly so in cold water and chloroform, insoluble in ether. It melts at  $109^\circ$ . The aqueous solution is neutral in reaction, and gives no precipitate with silver nitrate. Heated with water, it is converted into an isomeric body which crystallises in needles belonging to the rhombic system; it melts at  $158^\circ$ , and is soluble in water and alcohol, insoluble in ether and chloroform. It forms a neutral aqueous solution, from which silver nitrate precipitates half the bromine present, thus proving the substance to be the hydrobromide of a brominated base. This substance has most probably one of the two following formulæ:—



From the neutral reaction of its aqueous solution, the author is inclined to regard the second as the more likely formula, for it seems improbable that a bromallylcarbamide would have such marked basic properties. *Bromopropylencarbamide hydrochloride* is obtained by digesting the hydrobromide with freshly precipitated silver chloride. It crystallises in concentrically-grouped needles, melting at  $143^\circ$ , and easily soluble in water and alcohol. The *platino-chloride*,



\* *Note by Abstractor.*—Maly (*Zeitschr. Chem.*, 1869, 261) states that allyl carbamide crystallises in prisms melting at  $241^\circ$ .

crystallises in orange-yellow scales, soluble in water, insoluble in absolute alcohol or ether. *Bromopropylencarbamide*,  $C_4H_7BrN_2O$ , is obtained from the hydrobromide by digesting it with silver oxide or by adding the calculated quantity of potassium hydroxide to its aqueous solution. It crystallises in well-formed silky needles which melt at  $120^\circ$ . It is sparingly soluble in cold water, easily so in boiling water, and forms a strongly alkaline solution. It dissolves in boiling alcohol, chloroform, and benzene, but crystallises out again, on cooling, in long needles. It forms neutral salts with acids. The *sulphate* is easily soluble in alcohol and water. With silver nitrate an aqueous solution of the free base gives a white precipitate soluble in nitric acid and ammonia; with mercuric chloride, it gives a heavy white flocculent precipitate. The author was unable to debrominate this base: tin and hydrochloric acid did not act on it, whereas the action of sodium-amalgam was too energetic and yielded no satisfactory results. Attempts to establish its constitution by decomposing it with alkalis or alcoholic ammonia, or by obtaining oxidation-products, also proved fruitless.

L. T. T.

**Action of Bromethylene on Benzene in Presence of Aluminium Chloride.** By HANRIOT and GUILBERT (*Compt. rend.*, 98, 525—526).—500 grams bromethylene were mixed with 230 grams benzene, and 20 grams aluminium chloride were added gradually to the cooled mixture in such a manner that the temperature did not rise above  $50$ – $60^\circ$ . No gases were evolved, and the product was thrown into ice-cold water, dried over potash, and distilled in a vacuum. Two fractions were thus obtained, one boiling at  $145$ – $150^\circ$  under a pressure of 0.03 m., and consisting of styrolyl bromide,  $C_6H_5.C_2H_4Br$ , the other boiling at  $200$ – $230^\circ$ , and consisting of dibromodiethylbenzene,  $C_6H_4(C_2H_4Br)_2$ . Above  $230^\circ$  no definite fraction could be obtained, and an abundant black tarry residue resulting from the decomposition of higher brominated products was left in the retort. These results are very different from those obtained by Angelbis and Anschütz (*Ber.*, 1884, 167).

C. H. B.

**New Compound formed in the Preparation of Benzene Hexchloride.** By J. MEUNIER (*Compt. rend.*, 98, 436—438).—When benzene hexchloride is prepared by the action of chlorine on boiling benzene purified from thiophene, and the crude product is sublimed, obtuse or acute lamellæ are first obtained, but towards the close of the operation small octahedral crystals condense in the receiver. These octahedral crystals melt at about  $300^\circ$  and volatilise immediately. They have no action on polarised light and belong to the cubic system, the observed faces, in addition to those of the octahedron, being those of the cube, tetrahedron, and triakistetrahedron.

The chemical properties of this new compound are analogous to but distinct from those of ordinary benzene hexchloride. It decomposes in the same manner above  $300^\circ$  into hydrochloric acid and trichlorobenzene, the latter being apparently identical with that obtained from the hexchloride. The new compound is, however, much less readily decomposed by alcoholic potash, and is not attacked by an

alcoholic solution of potassium cyanide. This latter property furnishes a method of separating the two substances.

The octahedral crystals are very soluble in benzene, but less soluble in alcohol. They have the composition  $x\text{C}_6\text{H}_6\text{Cl}_6$ , and are probably a polymeride of ordinary benzene hexachloride. C. H. B.

**Nitriles and Carboxylic Acids from Aromatic Amines.** By K. GOUSIOROWSKI and V. MERZ (*Ber.*, **17**, 73—74).—If formanilide is boiled alone, very little benzonitrile is produced, but the reaction is assisted by the addition of zinc-dust:  $\text{NPh.COH} + \text{Zn} = \text{NPhC} + \text{ZnO} + \text{H}_2$ , and  $\text{NPhC} = \text{PhCN}$ . The production of benzonitrile may also be effected by passing formanilide vapour over zinc-dust heated nearly to dull redness, the distillate consisting of benzonitrile and aniline. Formorthotoluide and formoparatoluide yield orthotolunitrile and paratolunitrile respectively. The results are confirmed by vapour-density determinations and conversion of the nitriles into the carboxylic acids. A. K. M.

**Action of Hydroxylamine on Nitriles.** By F. TIEMANN (*Ber.*, **17**, 126—129).—When an aqueous solution of hydroxylamine hydrochloride with an equivalent quantity of sodium carbonate is agitated with a concentrated ethereal solution of benzaldehyde cyanhydrin, crystals of an addition compound,  $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2$ , gradually form at the surface of contact of the two solutions. It is sparingly soluble in cold, readily in hot water, is insoluble in benzene, sparingly soluble in ether, very readily in alcohol. It melts at  $140^\circ$ , and at a higher temperature suddenly decomposes with evolution of gas and formation of benzaldehyde. With the view of ascertaining if this compound still contained the cyanogen-group, it was submitted to the action of concentrated sulphuric and hydrochloric acids, but with negative results, the substance being recovered unchanged on dilution and neutralisation. It behaves as an amido-acid, dissolves with the greatest readiness in both acids and alkalis, and is reprecipitated on neutralising the solutions. It forms a sparingly soluble crystalline platinum-chloride, and yields white crystalline precipitates on adding barium chloride, zinc sulphate, lead acetate, and silver nitrate to its ammoniacal solution, and a green precipitate with copper sulphate. Its neutral solution is coloured blood-red by ferric chloride; it is not reduced by Fehling's solution. It yields an acetyl-derivative melting at  $149^\circ$ , and a benzoyl-derivative melting at  $137^\circ$ . An addition-compound of hydroxylamine with benzonitrile,  $\text{C}_7\text{H}_8\text{N}_2\text{O}$ , can also be obtained, thus: an alcoholic solution of hydroxylamine hydrochloride is treated with the equivalent quantity of sodium carbonate in aqueous solution and benzonitrile added, together with sufficient alcohol to form a clear solution. The mixture is heated for some hours at  $60\text{--}80^\circ$ , when the odour of benzonitrile disappears, and on then evaporating the solution, a heavy oil separates, solidifying to a crystalline mass. It crystallises from water in prisms melting at  $70^\circ$ , and volatile without decomposition; it dissolves sparingly in cold, readily in hot water, alcohol, ether, and benzene. It is very readily dissolved by acids and alkalis, and shows a similar behaviour to the


above compound obtained from benzaldehyde cyanhydrin. The hydrochloride crystallises in concentrically grouped needles, and yields a moderately soluble platinochloride. Its aqueous solution is neutral, is coloured red by ferric chloride, and is not reduced by Fehling's solution. Its ammoniacal solution yields crystalline precipitates with barium chloride, zinc sulphate, lead acetate, and silver nitrate, and in the last case a silver mirror is obtained on warming. This condensation-product can only be represented by one of the formulæ,  $\text{NH}:\text{CPh.NH.OH}$  or  $\text{NH}_2.\text{CPh}:\text{N.OH}$ , and must therefore be either benzenyloxamidine or benzenylamidoxime. The condensation-product from benzaldehyde cyanhydrin and hydroxylamine would then be either phenyloxethenyloxamidine,  $\text{CHPh(OH).C(CNH)NHOH}$ , or phenyloxethenyamidoxime,  $\text{CHPh(OH).C(NH}_2\text{)N.OH}$ .

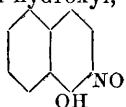
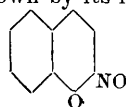
A. K. M.

**Nitrosophenols.** By H. GOLDSCHMIDT (*Ber.*, 17, 213—217).—The author has already described the action of hydroxylamine on various diketones and quinones (*Ber.*, 16, 2176). He now considers its action on benzoquinone and  $\beta$ -naphthaquinone.

Concentrated solutions of hydroxylamine hydrochloride and benzoquinone react so violently that the product is carbonised. Good results were obtained as follows:—1 part of quinone was dissolved in 300 parts water and an aqueous solution of 1 part hydroxylamine hydrochloride added; the dark-coloured liquid was allowed to stand until all odour of quinone had disappeared (about 12 hours), then shaken with animal charcoal, filtered, and extracted with ether. The ethereal solution was evaporated, and the liquid residue, after further treatment with animal charcoal, placed in a vacuum, when long colourless needles separated. These proved to be identical with the paranitrosophenol of Baeyer and Caro (*this Journal*, 1875, 84). As this method of formation throws some doubt on the constitution assigned to this compound, experiments are being made to ascertain its true nature.

$\beta$ -Naphthaquinone, when treated with hydroxylamine hydrochloride in manner similar to that described above, yields the  $\beta$ -nitroso- $\alpha$ -naphthol described by Fuchs (*this Journal*, 1876, 248). This substance, when heated in alcoholic solution with hydroxylamine hydrochloride and a few drops of hydrochloric acid in sealed tubes at  $130^\circ$ , yields a

substance of the formula  $\text{C}_{10}\text{H}_6$  , which crystallises in fine pale yellow needles, and melts at  $78^\circ$ . That this substance is an anhydride and does not contain hydroxyl, is shown by its insolubility in alkalis.

Of the two formula  and  that may be as-

signed to Fuchs' compound, the author regards the second as best explaining its reaction with hydroxylamine. He hopes soon to be able to settle the question.

A. J. G.

**Azoparacresol.** By C. LIEBERMANN and ST. V. KOSTANECKI (*Ber.*, 17, 130—132).—Liebermann previously pointed out the incorrectness of the view that in the formation of the azophenols, the azo-group always assumes the para-position to the hydroxyl (*Ber.*, 16, 2858), and he alluded to the formation of an azo-derivative of paracresol by Mazzara (*Gazzetta*, 9, 424, and *Abstr.*, 1880, 163). The authors have followed Mazzara's instructions in the preparation of the azo-derivatives of phenol and of the cresols, and they find that two compounds are almost always simultaneously produced, of which one is soluble and the other insoluble in dilute alkali. The two products are not isomerides, neither are the insoluble compounds always diazo-derivatives. *Phenylazo-paracresol*,  $\text{PhN}_2\text{C}_6\text{H}_3\text{Me.OH}$ , was prepared according to Mazzara's instructions, and the product dissolved in dilute alkali instead of in ammonia, and the solution precipitated with acetic acid. After repeated crystallisation from dilute alcohol, it was obtained in scales of a golden lustre melting at  $108^\circ$ ; it can be volatilised almost unchanged by careful heating. It dissolves completely in cold alkali, forms a brownish-red solution with concentrated sulphuric acid, and is readily soluble in cold alcohol. It colours animal fibre pale canary-yellow. On dissolving the portion insoluble in alkali, in sodium ethylate and adding water, it is obtained in brown needles, which may be purified by crystallisation from dilute alcohol. *Phenylazorthocresol* is prepared in the same way as the para-compound, and forms needles or scales of golden lustre melting at  $128\text{--}130^\circ$ . It is completely soluble in cold alkali, dyes wool yellow, and forms a brown solution with sulphuric acid. A substance insoluble in alkali is also produced. *Cumylazoresorcinol*,  $\text{C}_6\text{H}_2\text{Me}_3\text{N}_2\text{C}_6\text{H}_3(\text{OH})_2$  (from liquid cumidine), has also been prepared, and here again dilute alkali separates a soluble from an insoluble product. The soluble compound,  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2$ , forms small red needles, dissolves in concentrated sulphuric acid with a greenish yellowish-brown coloration, and melts a little above  $200^\circ$  with decomposition. The insoluble compound is possibly *cumylazoresorcinolazocumyl*,  $(\text{C}_6\text{H}_2\text{Me}_3\text{N}_2)_2\text{C}_6\text{H}_2(\text{OH})_2$ .

A. K. M.

**Constitution of Resocyanin.** By A. MICHAEL (*Am. Chem. J.*, 5, 434—440).—After alluding to papers by Wittenberg, W. Schmid, and H. v. Pechman and C. Duisberg, the author describes his independent observations made some time ago.

The body was obtained by heating together equal weights of ethylic acetoacetate, resorcinol, and zinc chloride, and pouring the product into cold water. Analyses of this preparation and also those analyses made by Pechmann and Duisberg would seem to point to the formula  $\text{C}_{10}\text{H}_8\text{O}_3$ , while the determinations of Schmid and of Wittenberg agree better with the formula  $\text{C}_{20}\text{H}_{16}\text{O}_6$ . Resocyanin is fluorescent. When heated with acetic anhydride and sodium acetate, acetyl-resocyanin is formed. The methyl-derivative was obtained by adding sodium methylate and methyl iodide to a solution of resocyanin in methyl alcohol. With hydrogen an addition-product is formed, and this, treated with acetic anhydride and sodium acetate, yields a crystalline monacetyl-derivative. An acetic acid solution of bromine gives with resocyanin a crystalline precipitate,  $\text{C}_{10}\text{H}_8\text{Br}_3\text{O}_3$ . Potassium perman-



ganate oxidises resocyanin completely in the cold; fused with zinc chloride, a red mass, a zinc-derivative of resocyanin is obtained; phosphorous pentachloride acts on resocyanin. A few analyses are given, which are not however sufficient to decide the composition of resocyanin. Further work is required. H. B.

**1 : 2 : 4 Orthoxylidine.** By O. JACOBSEN (*Ber.*, **17**, 159—162).—Wroblewsky has described (*Abstr.*, 1881, 433) a xylidine which, without stating his evidence, he assumes to be the orthoxylidine 1 : 2 : 4. As from the method by which it was prepared it seemed probable to the author that it was a somewhat impure paraxylidine, he has prepared the 1 : 2 : 4 orthoxylidine, and finds it to be a substance entirely different from that described by Wroblewsky.

*Nitro-ortho-xylene*,  $C_6H_3MeMe.NO_2$  [1 : 2 : 4], is prepared by slowly adding pure orthoxylene to 8 or 10 times the quantity of fuming nitric acid, the mixture being kept well cooled. After purification, orthoxylidine is obtained as a yellowish heavy oil, which solidifies on cooling. It crystallises from alcohol in long clear yellow prisms, and melts at 29°. It boils with slight decomposition at 258° under the ordinary pressure, and without decomposition at 248° under 580 mm. pressure. Its sp. gr. is 1.139 at 30° (water at 30° = 1). It is the only nitroxylene produced in appreciable quantity by the reaction.

*Orthoxylidine*,  $C_6H_4Me_2.NH_2$  [Me : Me :  $NH_2$  = 1 : 2 : 4], is best prepared from nitro-ortho-xylene by reduction with tin and hydrochloric acid; it crystallises in forms belonging to the monoclinic system, has scarcely any odour, melts at 49°, and boils at 226°. Its sp. gr. at 17.5 = 1.0755. It is sparingly soluble in cold water, moderately in light petroleum, readily in alcohol and ether. Pure orthoxylidine remains colourless when exposed to air and light.

*Orthoxylidine hydrochloride*,  $C_6H_4N.HCl + H_2O$ , crystallises in long thin prisms, is readily soluble in water, sparingly soluble in hydrochloric acid. It begins to volatilise at a little above 100°.

*Acetoxylide*,  $C_6H_5.NHAc$ , prepared by heating orthoxylidine with glacial acetic acid and acetic chloride, or by several hours' heating with glacial acetic acid alone, crystallises in brilliant long thin prisms, melts at 99°, is sparingly soluble in cold water, readily in alcohol.

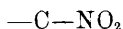
The constitution of orthoxylidine was proved by its conversion into 1 : 2 : 4 orthoxylene. This latter substance melts at 62.5°, not 61° as previously stated by the author (*Abstr.*, 1878, 412).

A. J. G.

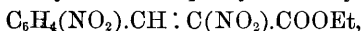
**Paramidobenzyl Cyanide.** By P. FRIEDLÄNDER (*Ber.*, **17**, 236—238).—A base of the formula  $C_6H_5N_2$  was observed by the author and Mähly (*Abstr.*, 1883, 918) to occur as a bye-product in the reduction of ethyl paranitrophenyl-nitroacrylate, and was erroneously supposed by them to have the constitution  $NH_2.C_6H_4.CH.N$ . Further inves-



tigation has, however, shown the substance to be *paramidobenzyl cyanide*,  $NH_2.C_6H_4.CH_2.CN$ , so that in the reaction the group,



must have been reduced to the cyanogen-group; a reaction that has not been previously noticed. The true nature of the substance was clearly shown by treatment with hydrochloric acid, when it yielded an acid agreeing in all particulars with those given for paramidophenylacetic acid by Radziszewski (*Ber.*, 2, 209), and by Bedson (*Trans.*, 1880, 92), and further by comparison with paramidobenzyl cyanide, prepared by reduction of paranitrobenzyl cyanide. In similar manner, by the reduction of ethyl metanitrophenylnitroacrylate,



with tin and hydrochloric acid, it yields metamidobenzyl cyanide.

A. J. G.

**Behaviour of Diamines towards Nitrous Acid.** By A. LADENBURG (*Ber.*, 17, 147—150).—The author has shown that the condensation-products obtained by the action of nitrous acid on the diamines differ according to the position of the amido-groups; the reaction product from the orthodiamines (the azinido-compounds) being derived from 1 mol. of the diamine only, whilst in the meta- and para-compounds the product is derived from 2 mols. (this *Journal*, 1876, 933; 1877, 302). Biedermann and Ledoux have, however, stated (*Ber.*, 7, 1531) that the nitrophenylenediamine melting at 195°, from which Hofmann prepared the first known azinido-compound, is identical with nitroparaphenylenediamine. The author therefore thought it necessary to reinvestigate the question. Paraphenylenediamine was converted into the acetyl-compound, and then nitrated; the resulting *nitro-diacetylparaphenylenediamine* crystallises in golden-yellow needles, and melts at 184°. On gently heating it with dilute soda solution, *nitromonacetylparaphenylenediamine*,  $\text{C}_6\text{H}_3(\text{NO}_2)(\text{NH}_2).\text{NH}\bar{\text{A}}\text{c}$ , is obtained, crystallising in red needles and melting at 186°. By boiling either the mono- or di-acetyl-compound with concentrated hydrochloric acid for 15 minutes, diluting and supersaturating with ammonia, *nitroparaphenylenediamine*,  $\text{C}_6\text{H}_3(\text{NO}_2)(\text{NH}_2)_2$ , is obtained; it crystallises in nearly black needles, having a strong green lustre, and melts at 137°, dissolves readily in dilute acids, and forms well characterised salts. Its non-identity with ordinary nitrophenylenediamine, melting at 195°, is therefore certain. Dissolved in sulphuric acid, and treated with sodium nitrite, it yields a brown powder, which was not further investigated.

When a solution of paraphenylenediamine hydrochloride is treated with potassium nitrite, it yields a brown powder, insoluble in all ordinary solvents, the figures obtained on analysis approximating to those required for the formula  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_3$ .

With regard to the constitution of the nitrophenylenediamines, the new body from paraphenylenediamine must have the positions



whilst the compound melting at 195° has been obtained from the dinitroaniline in which the nitro-groups are in the meta-position to one another, its nitro- and amido-groups must occupy the positions  $[\text{NH}_2 : \text{NH}_2 : \text{NO}_2 = 1 : 2 : 4]$ . This latter body yields an acetyl-derivative,  $\text{C}_6\text{H}_3(\text{NO}_2)(\text{NH}\bar{\text{A}}\text{c})_2$ , crystallising in colourless needles.

A. J. G.

**Action of Hydroxylamine on the Imidoethers and Amidines.**

**Acidoximes.** By A. PINNER (*Ber.*, **17**, 184—186).—The imide-group in the imidoethers and amidines is readily converted into the oximido-group ( $\text{:N.OH}$ ) by the action of hydroxylamine. *Benzoximidether*,  $\text{CPh(OEt):N.OH}$ , is prepared by dissolving hydroxylamine hydrochloride in water, adding an equivalent quantity of benzimidether, together with as much alcohol as is necessary to give a clear solution; after standing for some days, the mixture is diluted with water and shaken with ether. On evaporation of the ethereal solution benzoximidether is left as a colourless liquid, which cannot be distilled without decomposition.

*Benzoxamidine*,  $\text{NH}_2\text{.CPh:N.OH}$ , is prepared by mixing equivalent quantities of the aqueous solutions of the hydrochlorides of benzamidine and hydroxylamine with addition of sufficient soda to decompose the latter salt, the mixture being allowed to stand some days; the like quantity of soda is again added, and the liquid extracted with ether. The residue from the evaporation of the ethereal solution is crystallised from alcohol, when large transparent plates of benzoxamidine are obtained melting at  $80^\circ$ . The substance shows great similarity in properties, except in melting point, with the addition-product of hydroxylamine and benzonitril melting at  $70^\circ$ , described by Tiemann (this vol., p. 734). A. J. G.

**Possible Number of Homologous and Isomeric Rosanilines.**

By A. ROSENSTIEHL and GERBER (*Compt. rend.*, **98**, 433—436).—The actual number of rosanilines already obtained is 9, 6 of which are homologues, the remainder being isomerides. It has been shown that the amines can be divided into three groups, according to their capability of forming rosanilines. Class (1) includes paratoluidine,  $\alpha$ -metaxyloidine, mesidine, and amidopentamethylbenzene, which furnish the carbon of the methane nucleus. In this class one of the  $\text{CH}_3$ -groups is in the para-position with respect to the  $\text{NH}_2$ -group, whilst the position of the other  $\text{CH}_3$ -groups is immaterial. Of the 20 known amidomethylbenzenes, only 10 fulfil these conditions. Class (2) includes aniline, orthotoluidine,  $\gamma$ -metaxyloidine, and other derivatives in which methyl is *not* in the para-position with respect to  $\text{NH}_2$ , but, in the case of homologues of aniline, *is* in the ortho-position. Class (3) includes those derivatives which do not contain methyl in the para- or ortho-position, and consequently yield no rosanilines.

There is no experimental evidence to show whether the presence of  $\text{CH}_3$  in the meta-position as well as in the ortho-position in a derivative of class 2 prevents the formation of a rosaniline. If it does not, the highest member of this class will be amidotetramethylbenzene ( $1 : 2 : 3 : 5 : 6$ ), and the highest rosaniline will be  $\text{C}_{31}\text{H}_{43}\text{N}_3\text{O}$ , formed by the action of 1 mol. amidopentamethylbenzene on 2 mols. amidotetramethylbenzene, and amongst the 20 known amidomethylbenzenes there are 8 ortho-derivatives and 10 para-derivatives, which together may form 80 homologous and isomeric rosanilines.

If, however the presence of  $\text{CH}_3$  in the meta-position in a member of class 2 does prevent the formation of a rosaniline, no tri-

methylbenzene can be in this group, since 1 of the 3  $\text{CH}_3$ -groups must be in the meta-position. The highest member of this class will therefore be  $\gamma$ -metaxyldine, and the total possible number of homologous and isomeric rosanilines will be 30, the number of homologues being 9, the highest of which will be  $\text{C}_{27}\text{H}_{35}\text{N}_3\text{O}$ . To distinguish between these various homologues and isomerides will probably be very difficult.

C. H. B.

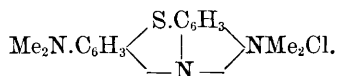
**Colouring Matters formed by the Simultaneous Oxidation of Paradiamines and Monamines.** By R. NIETZKI (*Ber.*, 17, 223—227).—By the oxidation of an acid solution of tetramethyldiamidodiphenylamine with ferric chloride, in presence of hydrogen sulphide, dimethylphenylene-green,  $\text{C}_{16}\text{H}_{20}\text{N}_3\text{Cl}$ , is first formed, and it is only after long standing and renewed addition of ferric chloride and of hydrogen sulphide that methylene-blue is obtained. The very small yield obtained, only 5 per cent. of the theoretical, points to its formation as due to some indirect process.

By oxidation of a mixture of equal molecular weights of paraphenylamine and diphenylamine, or of para-monamidodiphenylamine either alone or in presence of aniline, a substance,  $\text{C}_{18}\text{H}_{15}\text{N}_3(?)$ , is obtained closely related to aniline-black, and is probably identical with "emeraldine," the incompletely oxidised aniline-black.

The formula of phenosafranine is  $\text{C}_{18}\text{H}_{12}\text{N}_4$ , as stated by Bindschedler (*Ber.*, 16, 864), and not  $\text{C}_{18}\text{H}_{16}\text{N}_4$ , that previously given by the author. The author cannot confirm Bindschedler's statement that 4 atoms of hydrogen are necessary to convert 1 mol. of safranine into the leuco-bases; by titration of a strongly acid safranine solution with stannous chloride it was found that only 2 atoms of hydrogen were required.

A. J. G.

**Methylene-blue.** By R. MÜHLAU (*Ber.*, 17, 102—103).—On repeating the analysis of the double salt of methylene-white with zinc chloride, the numbers obtained indicate that this base has the formula  $\text{C}_{16}\text{H}_{19}\text{N}_3\text{S}$ , in accordance with the view held by Bernthsen (*Ber.*, 16, 2896), and not  $\text{C}_{16}\text{H}_{21}\text{N}_3\text{S}$ , as previously assumed by the author (*Ber.*, 16, 2728). He believes, with Bernthsen, that methylene-white is a tetramethyldiparamidodithiodiphenylamine, and that the hydrochloride of methylene-blue has the constitution



The atomic grouping assigned by Erlenmeyer to Bindschedler's dimethylphenylene-green (*Ber.*, 16, 2857) more probably represents the base,  $\text{C}_{16}\text{H}_{19}\text{N}_3$ , obtained by the author from nitrosodimethylaniline and dimethylaniline.

A. K. M.

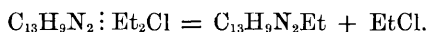
**Blue Colouring Matter from Pyrroline.** By G. CIAMICIAN and P. SILBER (*Ber.*, 17, 142—143).—The independent discovery of this substance by V. Meyer (this vol., 587), has obliged the authors to publish their researches on this subject, although still incomplete.

The best yield is obtained by dissolving 2 parts of isatin in 50 parts of glacial acetic acid, and adding 1 part of pyrroline to the boiling solution. The dark blue liquid is poured into water and nearly neutralised with sodium carbonate, when the colouring matter is precipitated. After purification, it forms a black microcrystalline powder, which assumes a metallic lustre when rubbed, has the composition  $C_{24}H_{18}N_4O_3$ , is insoluble in ether, soluble in glacial acetic acid, phenol, boiling alcohol, and concentrated sulphuric acid. Its formation is represented by the equation  $C_{16}H_{10}N_2O_4 + 2C_4H_5N - H_2O = C_{24}H_{18}N_4O_3$ .  
A. J. G.

**Ethyl Derivatives of Anhydrobenzodiamidobenzene.** By J. L. HOWE (*Amer. Chem. J.*, 5, 418—424).—When anhydrobenzodiamidobenzene is heated with ethyl iodide at  $120^\circ$ , it yields a mass consisting approximately of equal parts of the iodide of the diethyl derivative and the hydriodate of the anhydro-base. From the aqueous solution of these iodides hot sodic hydrate completely precipitates the anhydro-base, whilst from the filtrate caustic potash precipitates *diethyl-anhydrobenzodiamidobenzene hydroxide*,  $C_6H_4 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NEt}_2(\text{OH}) \end{array} \text{CPh}$ , a crystalline solid, melting at  $136^\circ$ . The following salts of this base are described: the iodide,  $C_{13}H_9N_2 : Et_2I, H_2O$ ; the chloride,



a second chloride containing one molecule of hydrochloric acid and several of water, crystallises imperfectly from a very concentrated acid solution; the platinochloride,  $(C_{13}H_9N_2Et_2Cl)_2PtCl_4$ , and the sulphate,  $C_{13}H_9N_2Et_2.HSO_4.H_2O$ ; all crystalline salts. When the chloride is heated above  $200^\circ$ , it gradually decomposes, and a thick oil distils over, which slowly becomes crystalline after purification; it is *ethyl-anhydrobenzodiamidobenzene*, and is formed thus,



This process could undoubtedly be applied to similar dialkyl anhydro-bases as a definite method of forming the monalkyl compounds which have hitherto been the result of no known conditions. The salts of this base are much less stable and less soluble in water than those of the diethyl base; boiling with dilute acid converts them into a salt of the anhydro-base. The hydrochloride,  $C_{13}H_9N_2Et.HCl, 3H_2O$ ; the platinochloride,  $[C_{13}H_9N_2Et]_2.H_2PtCl_6$ ; and the nitrate



are described. A table showing the formulæ and general properties of all the derivatives of anhydrobenzodiamidobenzene, as described in the present paper, and previous ones by Hübner, C. S. Merrick, and F. Rinne is appended.  
H. B.

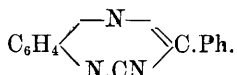
**A Nitrile of Anhydro-benzodiamido-benzene.** By J. L. HOWE (*Amer. Chem. J.*, 5, 415—418).—When anhydro-benzodiamido-benzene

(benzenyl-phenylene-amidine of Beilstein),  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{N} \diagdown \\ \diagdown \text{NH} \diagup \end{array} \text{Ph}$ , is heated

in a closed tube with an excess of cyanogen iodide, and a considerable quantity of benzene at about  $100^\circ$ , dark red crystals of the tri-

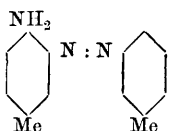
iodide,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{N} \diagdown \\ \diagdown \text{NH.HI} \diagup \end{array} \text{CPh.I}_2$  are formed, whilst the benzene contains

a substance,  $\text{C}_{13}\text{H}_9\text{N}_2.\text{CN}$ , forming pale-yellow crystals. When this is boiled with caustic potash, the original anhydro-base is regenerated, and ammonia and potassium carbonate are formed. It was not possible to replace the cyanogen-group by carboxyl by heating with water at  $250^\circ$ , nor by treatment with very concentrated hydrochloric acid in a freezing mixture. On attempting to convert the cyanogen-group into the methyleneamine group by the use of sodium-amalgam and water, the anhydro-base alone was obtained. It is therefore probable that the cyanogen group is not united to a carbon-atom, so that its constitution may be represented by the formula



The compound is probably a cyanamide, anhydro-benzdiamo-benzene cyanamide, but it shows no tendency to polymerise. H. B.

**Orthamidoazo-compounds.** By E. NÖLTING and O. N. WITT (*Ber.*, 17, 77—82).—The authors prove the incorrectness of the view that the formation of amidoazo-compounds from diazo-compounds and an amine only takes place when the para-position in the latter is free to the entrance of the azo-group. Hofmann and Geyger, and also Nietzki, could obtain no amidoazo-derivative from paratoluidine, a diazoamido-compound alone being formed, whilst orthotoluidine yields directly amidoazotoluene, according to Nietzki, without the intermediate production of the diazoamido-derivative. The authors find that perfectly pure orthotoluidine does yield a well-crystallised pale-yellow diazoamido-derivative; also that amidoazoparatoluene may be obtained if diazoamidoparatoluene (1 mol.) be added to 5—6 parts of melted paratoluidine, then dry paratoluidine hydrochloride (1 mol.), and the mixture heated for 10—12 hours at  $65^\circ$ . It crystallises in splendid orange-red lustrous needles, melting at  $118.5^\circ$ , is readily soluble in hot alcohol and ethyl acetate, very readily in benzene. Its salts are pale-yellow in the solid state, green in solution; the hydrochloride crystallises in slender, whitish-yellow needles, the acetyl-derivative,  $\text{C}_6\text{H}_4\text{Me.N}_2.\text{C}_6\text{H}_3\text{Me.NHAc}$ , in yellow needles, melting at  $157^\circ$ , and the benzoyl-derivative in orange-yellow needles, melting at  $135^\circ$ . Amidoazoparatoluene hydrochloride yields a disulphonic acid with fuming sulphuric acid, which is a yellow dye; by the action of nitrous acid on this and on amidoazoparatoluene, diazo-derivatives are produced, which yield red dyes with  $\beta$ -naphthol and its sulphonic acids. By the action of reducing agents on amidoazoparatoluene, paratoluidine and orthotolylenediamine are obtained, proving the

constitution , and thus showing that the diazo-group

is capable of assuming the ortho-position when the para-position is occupied. The reaction also takes place with other substances, such as paradi-tolylamine.

On heating amidoazoparatoluene with paratoluidine hydrochloride dissolved in paratoluidine at 90—100°, a substance is produced resembling azophenine (Trans., 1883, 115). The *azophenine of paratoluidine*,  $C_{12}H_{11}N_3$ , crystallises in flat red needles, which melt at a high temperature, with decomposition. It dissolves in concentrated sulphuric acid, with reddish-violet coloration, and is insoluble in alcohol and ether. It is probably related to the substance obtained by Barsilowski (*Annalen*, **207**, 105) by the direct oxidation of paratoluidine. Dyes of the indulin series can be obtained from amidoazoparatoluene and the salts of primary bases. A. K. M.

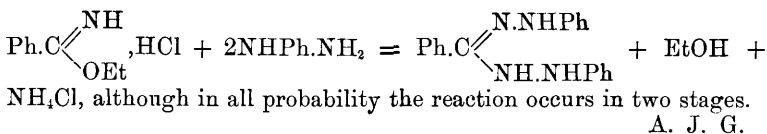
**Indulines.** By O. N. WITT (*Ber.*, **17**, 74—76).—In the ordinary method of producing the indulines, ammonia is produced, together with complicated secondary products, as previously shown by Witt and Thomas (Trans., 1883, 115). The author finds that this is not the case if phenylated amidoazobenzene be employed in the place of amidoazobenzene. On heating phenylamidoazobenzene (*Ber.*, **12**, 259) with aniline hydrochloride, no ammonia, and apparently no complicated secondary products are obtained, the reaction taking place more readily than when amidoazobenzene is used. The same applies to the higher homologues of phenylamidoazobenzene. The product of the action of diazoparatoluene on diphenylamine forms yellow plates, melting at 109—110°, and soluble in concentrated sulphuric acid with green coloration; the corresponding derivative of 1 : 2 : 4 metaxyline forms scales of golden lustre, melting at 142—143°, and yielding a yellow solution with concentrated sulphuric acid. On substituting other secondary aromatic amines for diphenylamine, amidoazo-derivatives are obtained, which yield a whole series of new induline-like dye-stuffs with the salts of primary bases. A. K. M.

**Indophenoles.** By O. N. WITT (*Ber.*, **17**, 76).

**Action of Phenylhydrazine on the Imido-ethers. Azidines.** By A. PINNER (*Ber.*, **17**, 182—184).—*Benzenyldiphenylazidine*,



is formed by the action of 2 mols. phenylhydrazine on 1 mol. benzyimido-ether hydrochloride, both in alcoholic solution, the mixture being allowed to stand for 24 hours. It crystallises in tufts of deep red needles, having a golden-yellow metallic lustre, and melts at about 170°. It is sparingly soluble in cold alcohol, readily soluble in hot alcohol and in benzene, the solutions having an intense red colour. The formation of the substance is represented by the equation



**Preparation of Orthonitrobenzaldehyde.** By A. EINHORN (*Ber.*, 17, 119—122).—This method depends on the oxidation of sodium ortho-nitrocinnamate by means of permanganate solution, and the removal of the resulting aldehyde at the moment of its formation from the oxidising liquid. It is carried out thus: 50 grams of crude orthonitrocinnamic acid are suspended in 2.5 litres water, neutralised with sodium carbonate solution, and filtered. The liquid is introduced into a large stoppered bottle, a litre of benzene added, and then little by little 1225 c.c. of a cold saturated solution of permanganate (6 per cent.), the mixture being vigorously agitated after each addition, and the whole kept cool by the introduction of ice. When the oxidation is finished, a warm solution of sodium sulphite (150 grams) is added, and then hydrochloric acid until the manganese dioxide is dissolved, when two layers are obtained, the lower of which is separated by means of a syphon. On distilling the benzene solution a liquid residue of orthonitrobenzaldehyde is obtained, crystallising on cooling. The yield by this method amounts to 50—53 per cent. of that required by theory, and in some experiments in which more dilute solutions were employed, and also more ice, the yield amounted to over 75 per cent., showing that the method is still capable of improvement.

A. K. M.

**Lactones.** By R. FITTIG (*Ber.*, 17, 201—203).—Phenylbutyrolactone unites with great readiness with hydrochloric, hydrobromic, or hydriodic acid when shaken with the aqueous acid saturated at 0°, yielding substitution-derivatives of phenylbutyric acid, identical with those obtained by similar treatment of isophenylcrotonic acid. They are reconverted into the lactone by the action of sodium carbonate.

An alcoholic solution of phenylbutyrolactone, when saturated with gaseous ammonia and evaporated over sulphuric acid, yields large colourless monoclinic crystals of a compound having the formula  $\text{C}_{10}\text{H}_{13}\text{NO}_2$ ; this melts at 85—86°, and at about 170° decomposes into lactone and ammonia. If crystallised from water, it can be obtained with 1 mol.  $\text{H}_2\text{O}$ . It dissolves in concentrated hydrochloric acid, but if excess of hydrochloric acid is added, a white crystalline precipitate of the hydrochloride is obtained; this redissolves on addition of a few drops of water, and after a few seconds the lactone precipitates. The hydrochloride dissolves completely in alcohol, but on spontaneous evaporation of the solution, is resolved into lactone and ammonium chloride. By gently heating the compound  $\text{C}_{10}\text{H}_{13}\text{NO}_2$  with alkalis, ammonia is evolved. The very ready decomposibility of this compound renders it doubtful whether it should be regarded as an amido-acid,  $\text{CHPh}(\text{NH}_2).\text{CH}_2.\text{CH}_2.\text{COOH}$ , or as an acid amide,



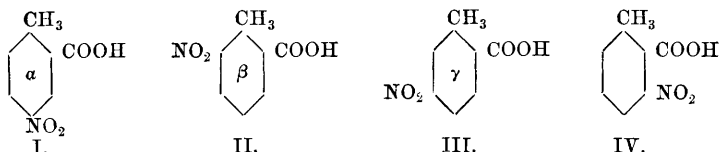
A. J. G.



**Nitro-orthotoluic Acids.** By O. JACOBSEN (*Ber.*, **17**, 162—164).

—The 1:2:4 nitro-orthoxylylene described in the Abstract, p. 737, yields a mixture of two nitro-orthotoluic acids, by oxidation with dilute nitric acid; these can be separated by conversion into the barium salts, the crystals differing so widely in form that a mechanical separation is readily effected. Of these acids, the one melting at 179° is identical with the  $\alpha$ -nitro-orthotoluic acid obtained by the nitration of orthotoluic acid; the other,  $\gamma$ -nitro-orthotoluic acid, melts at 152°, and is not identical with either of the acids obtained by the nitration of orthotoluic acid.

Of the four possible formulæ for orthonitrotoluic acids, the fourth



cannot belong to any of the three known acids, as none of them yield the hydroxy-acid. The  $\gamma$ -acid alone yields a hydroxy-acid (metahomoparahydroxybenzoic acid) that can be split up by hydrochloric acid; it is therefore represented by formula III. The  $\alpha$ -acid is obtained both by nitration of orthotoluic acid and by nitration of 1:2:4 nitro-orthoxylylene; it therefore must have the constitution shown by the first formula. The hydroxy-acid obtained from it agrees in all properties with parahomometahydroxybenzoic acid. (The author's earlier statement (*Ber.*, **16**, 1958) on this subject is erroneous.) There remains for the  $\beta$ -acid the second formula.

The properties of the three orthonitrotoluic acids are compared in the following table:—

$\alpha$ -Nitro-orthotoluic acid, [Me : COOH : NO<sub>2</sub> = 1 : 2 : 4], obtained together with the  $\beta$ -acid by nitration of orthotoluic acid; together with the  $\gamma$ -acid by oxidation of nitroorthoxylylene, melts at 179°.

The barium salt forms a soft opaque mass, composed of minute needles.

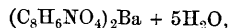
$\alpha$ -Amido-orthotoluic acid melts at 196°, and on treatment with nitrous acid yields parahomometahydroxybenzoic acid melting at 172°.

$\beta$ -Nitro-orthotoluic acid, [Me : COOH : NO<sub>2</sub> = 1 : 2 : 6], obtained, together with the  $\alpha$ -acid, by nitration of orthotoluic acid, melts at 145°.

$\beta$ -Amido-orthotoluic acid melts at 191°.

$\gamma$ -Nitro-orthotoluic acid, [Me : COOH : NO<sub>2</sub> = 1 : 2 : 5], obtained, together with the  $\alpha$ -acid, by oxidation of orthonitroxylylene, melts at 152°, crystallises in long lustrous needles, and is readily soluble in hot water and alcohol.

The barium salt,



crystallises in large transparent flat prisms.

$\gamma$ -Amido-orthotoluic acid melts at 165°, crystallises in long flat needles, and on treatment with nitrous acid yields metahomoparahydroxybenzoic acid melting at 179°. This latter, on heating at 200° with hydrochloric acid, is resolved into carbonic anhydride and metacresol.

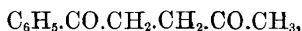
A. J. G.

**Action of Chlor- and Brom-acetone, Acetophenone Bromide, and Phenylbromacetic Acid on Ethyl Acetoacetate.**

By A. WELTNER (*Ber.*, **17**, 66—73).—Bromo- and chlor-acetone react readily with ethyl acetoacetate, but the author has not succeeded in obtaining any definite results; on saponifying the oily product ( $\text{CH}_2\text{Ac}.\text{CHAc}.\text{COOEt}$ ?) with cold dilute potash and acidulating, a brown oil is obtained, which becomes resinified on warming with dilute alkalis or by treatment with baryta-water. The preparation of ethylic acetophenone-acetoacetate from acetophenone bromide and ethyl acetoacetate has been described by Paal (this vol., 598). On reducing it with sodium-amalgam (the solution being kept neutral or slightly alkaline by the addition of acetic acid), a hydroxylactone,

$\text{OH}.\text{CHMe}.\text{CH} < \begin{smallmatrix} \text{CH}_2 \\ \text{COO} \end{smallmatrix} > \text{CHPh}$ , is produced; it forms a thick yellow

oil, insoluble in alkaline carbonates, soluble in alkalis and in baryta-water. When ethylic acetophenoneacetoacetate is boiled with dilute hydrochloric acid, much resinous matter is formed, together with a substance of the formula  $\text{C}_{11}\text{H}_{12}\text{O}_2$ ; it is obtained as a brownish-yellow oil, insoluble in dilute alkali, and decomposed on distillation in a vacuum. It is doubtful whether it is the diketone,



or the isomeric lactone. By the action of sodium-amalgam on an alcoholic solution, a deep brown-red colour is gradually produced, which disappears as the action continues, and on acidulating the colourless liquid, an acid ( $\text{C}_{12}\text{H}_{10}\text{O}_3$  or  $\text{C}_{12}\text{H}_{12}\text{O}_3$ ) is precipitated in white crystalline flakes; it crystallises from dilute alcohol in slender white lustrous needles melting at  $179^\circ$ . It is a well-characterised acid, dissolves readily in dilute alkalis, alkaline carbonates, and baryta-water; the sodium salt forms readily soluble lustrous needles, the silver salt a white insoluble precipitate. Boiled with acetic anhydride, it yields a compound insoluble in alkalis, sparingly soluble in alcohol, and crystallising from it in lustrous needles melting at  $139^\circ$ . Ethyl phenylacetosuccinate obtained from ethyl phenylbromacetate and ethyl acetoacetate has been prepared by Rügheimer (*Abstr.*, 1881, 600). It forms colourless lustrous scales melting at  $75-76^\circ$ , the free acid forming clusters of large plates melting at  $120-121^\circ$ ; the sodium salt crystallises in needles readily soluble in water. The monethyl-derivative,  $\text{COOH}.\text{CHAc}.\text{CHPh}.\text{COOEt}$ , forms slender needles melting at  $132.5^\circ$ . The ketonic acid,  $\text{CH}_2\text{Ac}.\text{CHPh}.\text{COOH}$ , is produced on boiling the mon- or di-ethyl-derivative with dilute hydrochloric acid or baryta-water; it is readily soluble in alcohol and ether, and crystallises in clusters of plates melting at  $126^\circ$ ; with nitric acid, it yields solid oxidation-products soluble in alkalis; a diketone has not yet been obtained from it. The zinc salt of the ketonic acid crystallises from hot water in long white needles; the silver salt forms a white flocculent precipitate; the copper salt, which is green, is insoluble in water, soluble in alcohol; the calcium and barium salts are readily soluble and do not crystallise. The lactone,

$\text{CHPh}.\text{CO} - \begin{array}{l} | \\ \text{CH}_2.\text{CHMe} \end{array} > \text{O}$ , is produced by the action of sodium-amalgam on the

ketonic acid, and forms an oil non-volatile (or nearly so) in steam. The calcium salt,  $(C_{11}H_{13}O_3)_2Ca \cdot H_2O$ , of the corresponding hydroxy-acid is readily soluble; the silver salt forms a white precipitate.

A. K. M.

**Derivatives of Orthonitrocinnamic Acid.** By J. M. MORGAN (*Ber.*, 17, 219—223).—Sodium orthonitrocinnamate (2 mols.) and sodium carbonate (1 mol.) are dissolved in water, and a stream of air saturated with bromine passed through the liquid. Orthonitrophenylbromolactic acid is the main product, but there is also formed an acid of the formula  $C_9H_9NO_6$ , crystallising in colourless transparent rectangular prisms, melting at  $94^\circ$ , and soluble in alcohol and ether. On dissolving it in hot anhydrous chloroform, water separates, and orthonitrophenyloxyacrylic acid is deposited on cooling.

On adding the acid  $C_9H_9NO_6$  to fuming hydrobromic acid, there are formed orthonitrophenylbromolactic acid, indigotine, and a substance which crystallises from hot glacial acetic acid in silky needles, is sparingly soluble in ether, alcohol, and water. The addition of the least excess of alkali to its solution causes the formation of a deep indigo-blue precipitate, whose colour is destroyed by acids. On diluting the filtrate, a yellow precipitate is obtained; it can be crystallised from acetone or acetic ether, and then forms brilliant scarlet rectangular prisms of the formula  $C_8H_7NO_2Br$  or  $C_{16}H_{10}N_2O_4Br_2$ , melts at  $255^\circ$ , and can be sublimed in long red needles on careful heating. It is sparingly soluble in chloroform, ether, and carbon bisulphide, more readily in alcohol.

A. J. G.

**Tetramethylbenzidine.** By W. MICHLER and H. PATTINSON (*Ber.*, 17, 115—119).—By the action of concentrated sulphuric acid on dimethylaniline, Michler and Salathé (*Ber.*, 12, 1171) obtained a base which was assumed to be either a tetramethyldiamidodiphenylmethane or tetramethylbenzidine,  $Me_2N \cdot C_6H_4 \cdot C_6H_4 \cdot NMe_2$ . The following experiments show that the latter view is the correct one:—A substance having the same properties is obtained by oxidising dimethylaniline dissolved in sulphuric acid, by means of lead dioxide; the reaction probably takes place thus:  $2C_6H_5NMe_2 + PbO_2 = NMe_2C_6H_4 \cdot C_6H_4 \cdot NMe_2 + PbO + H_2O$ . When benzidine dissolved in benzene, or better in methyl alcohol, is heated with methyl iodide in sealed tubes for some hours at  $120^\circ$ , the compound  $Me_2N \cdot C_6H_4 \cdot C_6H_4 \cdot NMe_3I$  is obtained. It melts at  $263^\circ$ , crystallises in needles, and is sparingly soluble in water and alcohol. On distilling it, tetramethylbenzidine is obtained, agreeing in melting point ( $195^\circ$ ) and all other properties with the above base and with that previously obtained by Michler and Salathé. The compound  $Me_2N \cdot C_6H_4 \cdot C_6H_4 \cdot NMe_3Cl$  is prepared by boiling the corresponding iodine-derivative in aqueous solution with freshly-precipitated silver chloride; it is readily soluble in water and alcohol, and crystallises from the former in yellowish crystals melting at  $228^\circ$ ; the platinochloride has the formula



*Dinitrotetramethylbenzidine*,  $C_{18}H_{18}N_2(NO_2)_2$ , is obtained as a yellowish-red precipitate on adding sodium nitrite to a solution of tetramethyl-

benzidine in dilute hydrochloric acid. It crystallises from alcohol in needles melting at  $188^{\circ}$ . On reduction, it yields *diamidotetramethylbenzidine*,  $C_{16}H_{18}N_2(NH_2)_2$ . This crystallises from alcohol in scales of silvery lustre, melts at  $168^{\circ}$ , and is readily soluble in hot, sparingly in cold alcohol, and insoluble in water. With ferric chloride and hydrochloric acid, it yields a violet coloration, which remains unaltered on dilution with water; and with potassium dichromate and sulphuric acid a brownish-red coloration, which becomes red on dilution; whilst permanganate and hydrochloric acid produce at first no change, the solution assuming a red coloration on standing.

A. K. M.

**New Method for producing Acridine.** By O. FISCHER and G. KÖRNER (*Ber.*, **17**, 101—102).—This consists in heating a mixture of chloroform (1 part), diphenylamine (1 part), zinc chloride (1 part), and zinc oxide ( $\frac{1}{2}$  part) for 7—8 hours at  $200$ — $210^{\circ}$ . The product is boiled with concentrated hydrochloric acid, the filtrate poured into water, and the acridine precipitated by alkali. The reaction,  $NHPh_2 + CHCl_3 + ZnO = C_{13}H_9N, HCl + ZnCl_2 + H_2O$ , is analogous to the formation of acridine from diphenylamine and formic acid (*Abstr.*, 1883, 1133), but the yield is considerably better. The base obtained by the authors melted at  $110$ — $111^{\circ}$ . Aluminium chloride may be substituted for the zinc chloride with advantage.

A. K. M.

**Acridine.** By L. MEDICUS (*Ber.*, **17**, 196—197).—Acridine nitrite,  $(C_{26}H_{18}N_2, NO_2H, H_2O)2H_2O$ , obtained by mixing solutions of potassium nitrite with an acridine salt, as a yellow flocculent precipitate, crystallises from hot water in long silky yellow needles, melts at  $150$ — $151^{\circ}$ , is sparingly soluble in cold water and in ether, more readily soluble in hot water, soluble in alcohol. The solutions show the fluorescence of acridine salts.

A. J. G.

**Chrysaniline.** By C. FISCHER and G. KÖRNER (*Ber.*, **17**, 203—209).—Very little more is known of this substance than was published by Hofman in 1862 and 1869 (*Compt. rend.*, **55**, 817; *Ber.*, **2**, 379). From its close resemblance to flavaniline, which has been recently shown by Fischer, Rudolph, and Besthorn (*Abstr.*, 1882, 1066; 1883, 600) to be a quinoline derivative, it appeared highly probable that chrysaniline would have a somewhat similar constitution: this view is now shown to be correct, as the authors' results prove chrysaniline to be the diamido-derivative of phenylacridine.

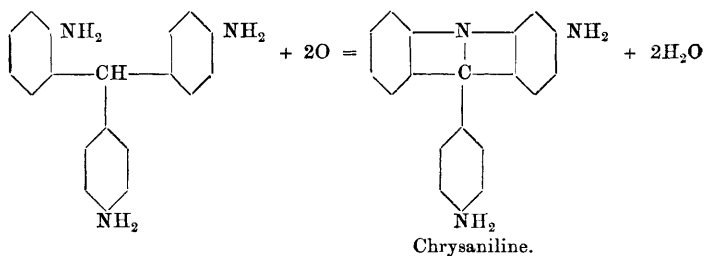
*Chrysophenol*,  $C_{19}H_{15}N_2O$ .—This substance was discovered and partly investigated by W. Claus, and further examined by the authors. By heating chrysaniline with 3—4 times its amount of concentrated hydrochloric acid at  $180^{\circ}$ , an amido-group is eliminated and replaced by hydroxyl,  $C_9H_{15}N_3HCl + H_2O = C_9H_{15}N_2O + NH_4Cl$ . Chrysophenol is separated from any unaltered chrysaniline by treatment with dilute soda in which it dissolves to a clear yellow solution, and is separated on neutralisation of the liquid as a yellowish-red precipitate. It crystallises from dilute alcohol in small red needles containing 1 mol.  $H_2O$ . It is sparingly soluble in water, benzene, and ether, very readily in alcohol. It is readily soluble in caustic alkalis,

but insoluble in alkaline carbonates. It still possesses strong dyeing powers and, like chrysaniline, forms sparingly soluble salts with acids. On oxidation, it yields a crystalline acid, and this when distilled with lime gives an intense odour of pyridine bases.

*Phenylacridine from Chrysaniline.*—10 grams chrysaniline is dissolved in a mixture of 50 grams sulphuric acid and 4–5 grams water, and the well-cooled solution treated with a stream of nitrous anhydride until distinct excess of the latter is apparent. The resulting diazo-compound is then added in small portions to 600 grams of boiling alcohol, when an intensely yellowish-green fluorescing liquid is obtained. The greater part of the alcohol is distilled off, water added, followed by excess of caustic soda, when reddish-coloured flocks separate, and without further purification are mixed with excess of soda, heated on an oil-bath at  $200^{\circ}$ , and distilled by aid of a current of steam, whilst the temperature of the bath is slowly raised to  $250^{\circ}$ . Phenylacridine distils over, and, after purification, shows all the properties described by Bernthsen and Bender (Abstr., 1883, 1133). The formation of phenylacridine from chrysaniline shows clearly that the formula of this latter must be  $C_{19}H_{15}N_3$ , and not  $C_{20}H_{17}N_3$ , that previously adopted.

With regard to the formation of chrysaniline in the rosaniline process, three views are possible. 1. That chrysaniline is a condensation-product from 2 mols. of aniline and 1 mol. of paramido-benzaldehyde obtained by oxidation of paratoluidine. 2. That it is a condensation-product from orthotoluidine and aniline. 3. That amido-phenylamine is formed, and reacts with amidobenzoic acid to form chrysaniline in a manner similar to that in which diphenylamine and benzoic acid yield phenylacridine.

Of these views the second is the most probable, as it is found that by heating orthodiparatriamidotriphenylmethane prepared from ortho-nitrobenzaldehyde and aniline (Renouf, Abstr., 1883, 981) with arsenic acid at  $180$ – $200^{\circ}$ , chrysaniline is formed:—



From these results chrysaniline must be regarded as *diamidophenylacridine*, the amido-groups being both in the para-position relatively to the methane carbon-atom.

A. J. G.

**Violet Derivatives of Triphenylmethane.** By O. FISCHER and G. KÖRNER (*Ber.*, 17, 98–101).—The authors describe a new synthesis of hexamethylparaleucaniline which lends support to their views on the violet derivatives of rosaniline, and also indicates a method for

the preparation of a whole series of methyl- and ethyl-derivatives of leucaniline. It consists in heating ethyl orthoformate (1 part) with dimethylaniline (3—4 parts) and zinc chloride (2 parts) for some hours on a water-bath, the zinc chloride being added gradually:  $\text{CH}(\text{OEt})_3 + 3\text{NPhMe}_2 = \text{CH}(\text{C}_6\text{H}_4\text{NMe}_2)_3 + 3\text{EtOH}$ .

The paper also contains a reply to Wichelhaus (*Ber.*, **16**, 3044).

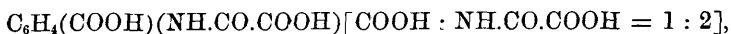
A. K. M.

**Kynuric Acid.** By M. KRETSCHY (*Monatsh. Chem.*, **5**, 16—32).—The author now finds that the above acid (*Abstr.*, 1883, 674) is identical with carbostyrylic acid, and not isomeric therewith as he formerly believed. The discrepancies previously observed in the behaviour of the two acids were due to inaccuracies in the published description of the properties of carbostyrylic acid. The kynuric acid used in the present research was prepared by the oxidation of kynurenic acid with an alkaline solution of potassium permanganate. The quantity of oxygen used in the oxidation was estimated and was always found to be about 6 atoms for every molecule of kynurenic acid oxidised. Small quantities of oxalic acid were usually formed, but scarcely any other by-products. The most favourable results were obtained under the following conditions:—20 grams of kynurenic acid and 10 grams crystallised potassium hydroxide ( $\text{KOH} + 2\text{H}_2\text{O}$ ) were dissolved in 3 litres of water, and 64 grams potassium permanganate in about one-fifth normal solution (*i.e.*, 3.5 grams  $\text{K}_2\text{Mn}_2\text{O}_8$  in 100 c.c.) added. The whole was kept at 60—70° for four days, and the acid was then precipitated with hydrochloric or nitric acid. Unchanged kynurenic acid was removed by treating the mixed acids with boiling ether, in which kynurenic acid is almost insoluble, kynuric acid being easily soluble. About 70 per cent. of the theoretical quantity of kynuric acid was thus obtained. The acid must be crystallised from luke-warm water only, as hot water causes partial decomposition.

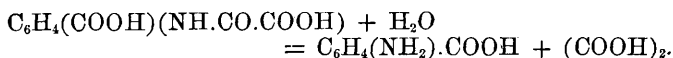
Kynuric acid crystallises in slender needles soluble in ether and alcohol, sparingly so in cold water (1 : 890 at 10°). The acid is dibasic, and forms acid and neutral salts. Its amido character is not very marked, but it forms double salts with platinum chloride, with iron chloride, and with silver and mercurous nitrates. It yields aniline when heated with a mixture of potassium hydroxide and carbonate. *Ammonium kynurate*,  $\text{C}_9\text{H}_5\text{NO}_5(\text{NH}_4)_2$ , crystallises in slender needles. *Hydrogen potassium kynurate* crystallises with  $\frac{1}{2}\text{H}_2\text{O}$ , and is sparingly soluble in water. *Hydrogen barium kynurate*,  $(\text{C}_9\text{H}_5\text{NO}_5)_2\text{Ba} + \text{H}_2\text{O}$ , is precipitated from a solution of the acid potassium salt by barium chloride, and crystallises in needles. *Barium kynurate*,  $\text{C}_9\text{H}_5\text{NO}_5\text{Ba} + \text{H}_2\text{O}$ , obtained from the neutral ammonium salt, forms microscopic needles, and gives up its water of crystallisation at 100°. *Calcium kynurate*,  $\text{C}_9\text{H}_5\text{NO}_5\text{Ca} + 2\frac{1}{2}\text{H}_2\text{O}$ , is precipitated in the form of microscopic needles which do not give up their water of crystallisation at 100°. A basic *copper* salt,  $2(\text{C}_9\text{H}_5\text{NO}_5\text{Cu}), \text{CuO} + 4\text{H}_2\text{O}$ , is precipitated from solutions of the neutral ammonium salt by copper acetate as a blue crystalline powder, which loses  $2\text{H}_2\text{O}$  at 100°.

When heated for some time at 189—191°, kynuric acid decomposes, giving off carbonic anhydride and water, and leaving a bitter residue,

sparingly soluble in benzene, ether, alcohol, and water. Alkalis dissolve it readily, and hydrochloric acid reprecipitates it from these solutions in a flocculent form. This residue seems to be a mixture of various bodies, and was not further examined. Kynuric acid cannot be crystallised from boiling water, as partial decomposition takes place. If its aqueous solution be maintained for some time at about  $100^{\circ}$ , or hydrochloric acid be added, and the solution be evaporated, the decomposition is complete, *orthamidobenzoic* and *oxalic* acids being produced. Friedländer and Ostermaier have already noticed this decomposition of carbostyric acid by hydrochloric acid. The formula of kynuric acid is therefore



and the decomposition takes place according to the equation:—



The author has succeeded in synthesising kynuric acid by heating together an intimate mixture of dry *orthamidobenzoic* and *oxalic* acids in an oil-bath at  $115$ — $135^{\circ}$ , and finally at  $145$ — $150^{\circ}$ . The acid thus obtained is identical with kynuric acid.

The formation of oxaly-*orthamidobenzoic* acid by the oxidation of carbostyryl, acetotetrahydroquinoline, kynurenic acid, and kynurin, and that of acetoanthranilic acid from quinaldine, shows the tendency of quinoline-derivatives to form anilido-compounds when the pyridine-ring is oxidised. The author intends to investigate the causes of potassium permanganate attacking the pyridine-ring in kynurenic acid and kynurin, and not the benzene-ring. From the results obtained by the oxidation, it is clear that the carboxyl and hydroxyl radicles in kynurenic acid are present in the pyridine-ring.

L. T. T.

**Derivatives of Naphthalene.** By E. LELLMANN (*Ber.*, **17**, 109—114).—By the action of nitric acid on  $\alpha$ -acetonaphthalide, the author obtained a nitro-product melting at  $171^{\circ}$  in accordance with the results obtained by Liebermann (*Annalen*, **183**, 229) and by Andreou and Biedermann (*Ber.*, **6**, 342), and by the action of potassium hydroxide on this,  $\alpha$ -nitronaphthylamine was produced. By the action of benzoic chloride on  $\alpha$ -nitronaphthylamine melting at  $190^{\circ}$ , the  $\alpha$ -nitrobenzonaphthalide, melting at  $224^{\circ}$  (Hübner and Ebell, *Annalen*, **208**, 324) is obtained, yielding naphthylenediamine (m. p.  $186^{\circ}$ ), on reduction. On reconvertng  $\alpha$ -nitronaphthylamine into the acetyl-derivative by means of acetic anhydride,  $\alpha$ -nitroacetonaphthalide is obtained melting at  $187^{\circ}$ , and crystallising in long yellow needles; also a small quantity of a second substance ( $\delta$ -nitroacetonaphthalide) melting at  $142^{\circ}$ . The mother-liquors from the preparation of  $\alpha$ -nitronaphthylamine gradually deposit crystals containing  $\beta$ - and  $\gamma$ -nitronaphthylamines which can be separated by crystallisation from alcohol. The  $\beta$ -compound forms small yellow needles, melting at  $198^{\circ}$ , and yields a benzoyl-derivative, melting at  $175^{\circ}$ , identical with Hübner and Ebell's benzoylorthonitronaphthalide

obtained by nitrating benzoynaphthalide. By the action of acetic anhydride on  $\beta$ -nitronaphthylamine,  $\beta$ -nitracetonaphthalide is obtained, melting at  $115^\circ$ .  $\gamma$ -Nitronaphthylamine melts at  $144^\circ$  and crystallises from alcohol in splendid prisms of the colour of potassium dichromate and of greenish lustre. It yields an *acetyl-derivative*, melting at  $194^\circ$ , and by the action of alkali on this,  $\gamma$ -nitronaphthol is produced, melting at  $116^\circ$ . The author has examined Liebermann's  $\gamma$ -nitroacetonephthalide, melting at  $190^\circ$ , and finds it to be identical with  $\alpha$ -nitroacetonephthalide, melting at  $187^\circ$ . It is not yet understood whether the four isomeric nitro-derivatives of  $\alpha$ -acetonephthalide are formed during the nitration and exist together in the product melting at  $171^\circ$ , or whether a molecular change occurs in the splitting off or introduction of the acetyl-group; a product melting at  $171^\circ$  could not be obtained from a solution containing  $\alpha$ - and  $\beta$ -nitroacetonephthalide. Nothing is known of the constitution of the  $\gamma$ - and  $\delta$ -derivatives; the  $\alpha$ -compound is without doubt



whilst the constitution of the  $\beta$ -derivative cannot yet be decided owing to the apparently contradictory nature of the necessary data. By the further nitration of  $\beta$ -nitroacetonephthalide a dinitro-derivative, melting at  $247^\circ$ , is produced identical with the compound obtained by Liebermann by the direct nitration of acetonephthalide, and the constitution of which is



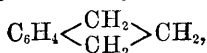
$\alpha$ -Nitroacetonephthalide appears to yield a different dinitro-derivative.

A. K. M.

**Derivatives of  $\beta$ -Dinaphthylamine.** By C. RIS and A. WEBER (*Ber.*, 17, 197—198).— $\beta$ -Dinaphthylamine is now obtainable in considerable quantities as it is a bye-product in the manufacture of  $\beta$ -naphthylamine. *Dinitro- $\beta$ -dinaphthylamine* is obtained by adding the base to a well-cooled mixture of fuming nitric acid and glacial acetic acid. It crystallises from cumene in yellowish-red needles or fine prisms, and melts at  $224$ — $225^\circ$ . *Tetranitro- $\beta$ -dinaphthylamine* is obtained together with the above, and is formed exclusively if the temperature rises during the reaction. It is very sparingly soluble in benzene or cumene, readily soluble in boiling nitrobenzene, from which it separates on cooling in yellow crystalline granules of melting point  $285$ — $286^\circ$ .

A. J. G.

**Derivatives of Hydrindonaphthene.** By A. BAEYER and W. H. PERKIN, Jun. (*Ber.*, 17, 122—125).—On treating orthoxylylene bromide with ethyl sodomalonate according to Perkin's method (*Ber.*, 16, 208, 1787, 2136), the ethyl dicarboxylate of a hydrocarbon,



is produced, which the authors name *hydrindonaphthene*, indonaphthene being  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{CH}$ , and bearing the same relation to indol



that naphthalene does to quinoline:  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH}_2\text{Br} \\ \text{CH}_2\text{Br}\end{smallmatrix}\rangle + \text{Na}_2\text{C}(\text{COOEt})_2 = \text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{C}(\text{COOEt})_2 + 2\text{NaBr}$ . The *orthoxylylene bromide* obtained by the authors must be isomeric with the compound described by Radziszewski and Wispeck (Abstr., 1882, 1284), since it melts at  $93^\circ$  and dissolves in 5 parts of ether. *Hydrindonaphthenedicarboxylic acid*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{C}(\text{COOH})_2$ , is best prepared as follows:—Sodium (2 atoms) is dissolved in 8 times its weight of alcohol, and the semi-solid mass obtained mixed with 3 times its weight of ether; a solution of the bromide (1 mol.) in 5 parts ether is next added, and then a solution of ethyl malonate (1 mol.) in the same quantity of ether. After standing three hours, the ether is decanted from the precipitate, and this, together with the residue from the evaporation of the ether, boiled with alcoholic potash until the addition of water no longer produces turbidity; the alcohol is evaporated, the residue dissolved in water, the solution filtered, acidulated with dilute sulphuric acid, and extracted with ether. Hydrindonaphthenedicarboxylic acid is moderately soluble in hot water from which it crystallises in rhombic plates melting at  $199^\circ$ , and then decomposing into carbonic anhydride and *hydrindonaphthenemonocarboxylic acid*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{CH}\cdot\text{COOH}$ . This melts at  $130^\circ$ , distils without decomposition, dissolves in 120 parts of boiling water, and very sparingly in cold water. A. K. M.

**Synthesis of Dimethylantracene Hydride and Diphenylethane from Benzene and Ethylidene Chloride.** By A. ANGEBLIS and R. ANSCHÜTZ (*Ber.*, 17, 165—167).—By the action of benzene on ethylidene chloride or bromide in presence of aluminium chloride, there are formed unsymmetrical diphenylethane and dimethylantracene hydride. Diphenylethane boils at  $150^\circ$  under 16 mm. pressure, is quite colourless, and has a blue fluorescence, its other properties are well known. Benzophenone boils at  $170^\circ$  under 15 mm. pressure.

*Dimethylantracene hydride* (diphenylene-diethylidine),  $\text{C}_{16}\text{H}_{16} = \text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CHMe} \\ \text{CHMe}\end{smallmatrix}\rangle\text{C}_6\text{H}_4$ , crystallises from solvents in pale yellow transparent plates, melts at  $178$ — $179^\circ$ , and sublimes readily in transparent clear yellow broad needles. It is readily soluble in ether, benzene, carbon bisulphide, boiling glacial acetic acid and hot alcohol. On oxidation with chromic acid, it yields anthraquinone and carbonic anhydride approximately in the ratio of 1 mol. of the former to 2 mols. of the latter. On distillation over nearly red hot zinc-dust the hydrocarbon readily yields anthracene. The picric acid compound,  $\text{C}_{16}\text{H}_{16}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}$ , crystallises in dark reddish-blue needles, and melts at  $170^\circ$ . A. J. G.

**Action of Aluminium Chloride on a Mixture of Benzene and Vinyl Bromide and of Benzene and Vinyl Tribromide.** By A. ANGEBLIS and R. ANSCHÜTZ (*Ber.*, 17, 167—168).—By passing

a regular stream of vinyl bromide vapour into a mixture of benzene and aluminium chloride gently heated on the water-bath, there is obtained a mixture of ethylbenzene, diphenylethane, and dimethylanthracene hydride. The formation of ethylbenzene instead of cinnamene is an instance of the nearly general rule that in this reaction instead of an unsaturated, the corresponding saturated aromatic hydrocarbon is formed. With regard to the formation of the other two hydrocarbons, which are the same as those described in the preceding abstract as obtained by the action of benzene on ethylidene chloride, &c., it appears to the authors to be most probable that during the reaction an addition of HBr to vinyl bromide takes place with consequent formation of ethylidene bromide, which then reacts as already described.

By the reaction of benzene on vinyl tribromide in presence of aluminium chloride, dibenzyl was obtained in moderate quantity.

A. J. G.

**Remarks on the Preceding Communications on Synthesis by Means of Aluminium Chloride.** By R. ANSCHÜTZ (*Ber.*, 17, 169—170).—In the syntheses of hydrocarbons from benzene and the halogen-derivatives of fatty hydrocarbons by aid of aluminium chloride, four kinds of condensation-products may be distinguished:—1. Those in which phenyl replaces the halogen in one molecule of the halogen-derivative of the fatty hydrocarbon. 2. Those in which more than one hydrogen-atom of one and the same benzene molecule is replaced by alkyl-groups. 3. Those in which two phenylene-groups are united to two carbon-atoms, which are also united to one another. 4. Those in which two phenylene-groups are united to two carbon-atoms not in union with one another.

A. J. G.

**Paramidofluorene.** By J. STRASBURGER (*Ber.*, 17, 107—108).—In a previous paper (this vol., 329) the author mentioned the formation of paramidofluorene by the distillation of the hydrochloride of paramidodiphenic acid with lime. He now confirms this by comparing the substance so obtained with paramidofluorene prepared from

fluorene. He prepares *paranitrofluorene*,  $\begin{array}{c} \text{C}_6\text{H}_4(\text{NO}_2) \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{---} \text{CH}_2$ , by adding

nitric acid (sp. gr. 1.4) to a cold saturated solution of fluorene in glacial acetic acid, and then heating to the boiling point. It melts at 154°, and on oxidation yields nitrodiphenylene ketone melting at 217—218°. On reduction, it yields paramidofluorene crystallising from dilute alcohol in grey or brown crystals melting at 124—125°; the somewhat lower melting point (123°) previously given is explained by the imperfect purification of the small quantity of the substance obtained from the amidodiphenic acid. Paramidofluorene from both sources yields an *acetyl-derivative* melting at 187—188°.

A. K. M.

**Borneol from Camphor.** By J. KACHLER and F. V. SPITZER (*Monatsh. Chem.*, 5, 50—54).—Jackson and Menke (*Amer. Chem. J.*, 1883, 270) state that if camphor (10 grams) be dissolved in ten times its weight of alcohol and one-third more (4 grams) than the theoretical

quantity of sodium be gradually added, the camphor is converted into borneol, 9·4 grams of the latter, or 94 per cent., being obtained. The authors have repeated these experiments, but can not confirm the results. Mixtures of camphor and borneol were obtained, the unchanged camphor always largely predominating.

As the separation of borneol from camphor is impracticable, this reaction does not form a means of preparing borneol. The product, analysed by treatment with phosphoric chloride (when borneol yields  $C_{10}H_{17}Cl$ , and camphor  $C_{10}H_{16}Cl_2$ ) was proved to contain 22·8 per cent. borneol, and 77·2 per cent. camphor.

L. T. T.

**Isomeric Campholurethanes.** By HALLER (*Compt. rend.*, **98**, 578—580).—The author has previously described (*ibid.*, **92**, 1511, and **94**, 86 and 869) a dextrogyrate campholurethane obtained from dextrogyrate borneol, and crystallising in dextrohemihedral crystals. By the same method, he has prepared a campholurethane from lævogyrate Ngai borneol from Shanghai. This borneol has the same melting point,  $198^\circ$ , as dextroborneol, and its rotatory power  $[\alpha]_D = -32^\circ 30'$ . The lævocampholurethane thus obtained melts at  $126-127^\circ$ , and its alcoholic solution has a lævorotatory power  $[\alpha]_D = -29\cdot9$ . It is deposited from its aqueous solution in lævohemihedral crystals, the dominant form being a rhomboidal prism of  $82^\circ 32'$ , modified on the angles *o* and *e*, and on the face *g*. The angles of these crystals correspond exactly with those of the right-handed form, but the crystals of dextrocampholurethane never have the face *e* on angles to the left, and the crystals of lævocampholurethane never have this face on angles to the right, and on most of the crystals the inverse law holds good for the face *g'*.

Dextroborneol yields a campholurethane which forms dextrohemihedral crystals, and is dextrogyrate, whilst lævoborneol yields a campholurethane which forms lævohemihedral crystals, and is lævogyrate. This dissymmetry is strictly analogous to that observed by Pasteur in the case of the sodium ammonium tartrates.

In the preparation of lævocampholurethane, a lævogyrate borneol carbonate is also obtained, and this compound is formed in much higher proportion than is dextrogyrate borneol carbonate from dextroborneol, in fact, the Ngai borneol is often almost entirely converted into the carbonate. It would seem, therefore, that the isomerism of this borneol with ordinary borneol is not purely physical, and this supposition is supported by the fact that in the preparation of lævocampholurethane a substance slightly soluble in alcohol and ether is formed, which is not formed in the preparation of the dextrocompound. Moreover, dextrocampholurethane melts at  $115^\circ$ , whilst the isomeric lævocampholurethane melts at  $126-127^\circ$ . The two borneol carbonates have, however, the same melting point,  $215^\circ$ .

C. H. B.

**Oxidation of Menthol by Potassium Permanganate.** By G. ARTH (*Compt. rend.*, **98**, 576—577).—8 grams of potassium permanganate, 500 c.c. of water, and 5 c.c. of dilute sulphuric acid (1 : 4) are placed in a stoppered flask, 4 grams of finely powdered menthol added, the mixture agitated and allowed to stand in a warm place.

After 24 hours a further quantity of 2 grams of menthol is added, and the addition is repeated at the end of 48 hours. When the permanganate has been decolorised, the liquid is neutralised with sodium carbonate and concentrated by evaporation. The sodium salt is then decomposed by dilute sulphuric acid, and the liquid agitated with ether, which on evaporation leaves a brown syrupy liquid, which does not distil at a fixed temperature, has a somewhat powerful odour slightly resembling that of valeric acid, and is only slightly soluble in water, to which it imparts a strongly acid reaction. This brown liquid seems to be a mixture of two distinct acids. It dissolves with effervescence in sodium carbonate solution, and if the excess of carbonate is removed by means of alcohol, and silver nitrate is added, two distinct precipitates are obtained. One of these dissolves in boiling water, and on cooling the solution deposits nacreous lamellæ of the composition  $C_{10}H_{17}AgO_3$ ; they are the silver salt of an acid  $C_{10}H_{15}O_3$ , which is liquid at ordinary temperatures. The other precipitate is not soluble in boiling water, but is gradually decomposed by prolonged ebullition. It is probably the silver salt of a more highly oxidised acid intermediate between the acid,  $C_{10}H_{15}O_3$ , and carbonic and oxalic acids.

C. H. B.

**Contributions to the Constitution of Brazilin.** By M. WIEDEMANN (*Ber.*, 17, 194—195).—By heating brazilin with amorphous phosphorus and hydriodic acid of sp. gr. 1.5 for some hours in a vessel provided with a reflux condenser, it yields *brazinole*,  $C_{16}H_{14}O_4$ , as a dark-brown amorphous powder, readily soluble in alcohol and alkalis, insoluble in benzene and chloroform, sparingly soluble in ether, water, and dilute acids. By heating brazilin or brazinole in sealed tubes with phosphorus and hydriodic acid of sp. gr. 1.9 at  $150^\circ$  for 8—12 hours, a substance of the formula  $C_{16}H_{26}O_3$  or  $C_{16}H_{24}O_3$  is obtained as a red-brown amorphous powder, resembling brazinole in its solubilities.

On distilling brazinole with zinc-dust in a stream of carbonic anhydride, nearly complete decomposition ensues, very minute quantities only of a crystalline substance, apparently a hydrocarbon of the formula  $C_{16}H_{14}$  or  $C_{16}H_{16}$ , being obtained.

By fusing brazilin with potash, Liebermann and Burg (*Ber.*, 9, 1883) obtained resorcinol; in the products of the fusion at  $240$ — $250^\circ$ , the author found formic and acetic acids, at higher temperatures ( $310$ — $330^\circ$ ) formic acid and resorcinol.

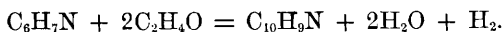
A. J. G.

**Quinoline and Quinaldine.** (*Dingl. polyt. J.*, 250, 533—542.)—When an aqueous solution of orthamidobenzaldehyde is treated with a small quantity of acetaldehyde and a solution of caustic soda, quinoline is produced. Friedländer and Gohring have found that this reaction is not limited to acetaldehyde, but that a large number of aldehydes and ketones give quinoline when treated with orthamidobenzaldehyde in a similar manner. Aqueous solutions of orthamidobenzaldehyde and pure acetone when treated in the cold with soda-ley combine together, producing  $\alpha$ -methylquinoline or quinaldine, a colourless oil of pleasant odour boiling at  $240^\circ$ .

According to the "Chemische Fabrik," formerly E. Schering of

Berlin, quinaldines are obtained on warming acetaldehyde with the salts of primary aromatic amines. The resulting bases can be converted into hydro- or hydroxy-derivatives, which may be used in dyeing or as antiseptic and antipyretic agents.

The simplest substitute of these bases, *i.e.*, quinaldine obtained from aniline and aldehyde is formed, according to the equation—



For the preparation of quinaldines, a mixture of 100 parts aniline (115 toluidine or 130 xylydine) 150 paraldehyde, 200 fuming hydrochloric acid, and 2—5 aluminium chloride, is boiled for 4 to 6 hours. The product is then poured into water, and the filtered solution saturated with soda-ley. The base produced is distilled with steam and purified by fractionation.

Aldehyde, acetal, crotonaldehyde, aldol, or lactic acid, may be employed in the place of paraldehyde, and hydrobromic, sulphuric, phosphoric, or other acids in the place of hydrochloric acid.

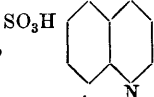
*Quinaldine*,  $\text{C}_{10}\text{H}_9\text{N}$  (from aniline), is a liquid resembling quinine in smell. It boils at  $240^\circ$ . *Orthomethylquinaldine*,  $\text{MeC}_{10}\text{H}_8\text{N}$ , is liquid, and boils at  $249\text{--}251^\circ$ . *Paramethylquinaldine* is isomeric with the former, but is solid, forming colourless crystals which melt at  $59\text{--}60^\circ$ .

When a mixture of aniline and ethyl acetoacetate is heated nearly to the boiling point, alcohol escapes. On interrupting the reaction when the mass becomes dark yellow, treating the product with concentrated sulphuric acid, diluting with water and adding alkali, *hydroxymethylquinoline*,  $\text{C}_{10}\text{H}_9\text{ON}$ , is precipitated (m. p.  $222^\circ$ ). D. B.

**Paradibromoquinoline.** By S. METZGER (*Ber.*, 17, 186—191).—*Paradibromoquinoline* is prepared by heating paradibromaniline with nitrobenzene, glycerol, and sulphuric acid. It crystallises in long white needles, can be distilled with steam, melts at  $127\text{--}128^\circ$ . It is nearly insoluble in water, readily soluble in acids, ether, alcohol, benzene, light petroleum, &c. The *hydrochloride*,  $\text{C}_9\text{H}_5\text{Br}_2\text{N}\cdot\text{HCl}$ , crystallises in small broad needles; it is decomposed into free base and hydrochloric acid by cold water. The *picrate* crystallises in long yellow needles, and is also decomposed by water. The *chromate*,  $(\text{C}_9\text{H}_5\text{Br}_2\text{N})_2\cdot\text{H}_2\text{Cr}_2\text{O}_7$ , forms a microcrystalline orange-red powder. The *platinochloride*,  $(\text{C}_9\text{H}_5\text{Br}_2\text{N})_2\cdot\text{H}_2\text{PtCl}_6$ , crystallises in minute yellow needles, and is readily decomposed by water. A comparison of the  $\alpha$ -dibromoquinoline obtained by La Coste (*Abstr.*, 1881, 741) by direct bromination of quinoline, showed its identity with parabromoquinoline.

A. J. G.

**Paraquinolinesulphonic Acids.** By J. HAPP (*Ber.*, 17, 191—193).—Ortho- and meta-quinolinesulphonic acids have been obtained by the action of sulphuric acid on quinoline (Lubavin, *Annalen*, 155, 313; Bedall and A. Fischer, *Abstr.*, 1882, 869).

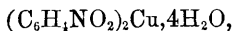
*Paraquinolinesulphonic acid*, , is obtained by heating

a mixture of sulphanilic acid, nitrobenzene, glycerol, and sulphuric acid. It crystallises in strongly refractive, hard, brilliant, colourless needles of the formula  $C_6H_5N.SO_3H + 1\frac{1}{2}H_2O$ , is sparingly soluble in cold water or cold alcohol, more readily soluble in hot water or alcohol. It does not melt at  $260^\circ$ . The barium salt,  $(C_6H_5SO_3N)_2Ba$ , forms crystalline scales; the potassium salt,  $C_6H_5NSO_3K$ , crystallises in brilliant plates; the sodium salt,  $C_6H_5NSO_3Na$ , crystallises in lance-shaped needles; the silver salt,  $C_6H_5NSO_3Ag$ , forms slender white needles; an acid silver salt,  $2C_6H_5NSO_3Ag + C_6H_7NSO_3$ , also crystallises in needles. On fusing the sulphonic acid with potash, a hydroxyquinoline of melting point  $193^\circ$  is obtained, apparently identical with Skraup's parahydroxyquinoline. A. J. G.

**Relation between Benzene and Pyridine.** By C. BÖTTINGER (*Ber.*, 17, 144).

**Pyridine-derivatives.** By C. BÖTTINGER (*Ber.*, 17, 92—95).—This paper contains the analytical data omitted in previous communications (*Abstr.*, 1881, 181 and 612). Picolinecarboxylic acid crystallises with 1 mol.  $H_2O$ , which it gradually loses in dry air, rapidly when heated at  $100^\circ$ . It forms a very readily soluble barium salt,  $(C_7H_6NO_2)_2Ba, 11H_2O$ , crystallising in broad lustrous needles, which effloresce on exposure to the air. The calcium salt,  $(C_7H_6NO_2)_2Ca, H_2O$ , is readily soluble in water, and crystallises in colourless transparent four-sided prisms, which do not lose their water at  $120^\circ$ . The sulphate and oxalate of picolinecarboxylic acid are readily soluble in water; the platinochloride crystallises in scales, readily soluble in water and alcohol.

Pyridinedicarboxylic acid crystallises with 1 mol.  $H_2O$ , which it readily loses at  $100^\circ$ : it dissolves readily in sulphuric and hydrochloric acids, but on evaporating the hydrochloride on a water-bath, the acid becomes dissipated. The barium salt,  $C_7H_3NO_4Ba, 1\frac{1}{2}H_2O$ , is sparingly soluble, and the calcium salt,  $C_7H_3NO_4Ca, \frac{1}{2}H_2O$ , almost insoluble in water. Pyridinemonocarboxylic acid, obtained by heating the above, yields a very characteristic copper salt,



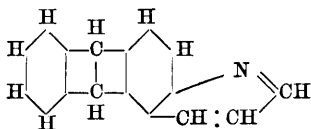
crystallising in bluish-green irregular six-sided scales. Tricarboxypyridinic acid (trimesitinic acid) yields a barium salt of the formula  $(C_8H_2NO_6)_2Ba_3, 7H_2O$ , and a calcium salt,  $C_8H_2NO_6Ca, 2\frac{1}{2}H_2O$ , insoluble in water and in dilute acetic acid; the copper salt,  $C_8H_3NO_6Cu, 3H_2O$ , forms an insoluble greenish-blue precipitate, and the silver salt,  $C_8H_2NO_6Ag_3, H_2O$ , a gelatinous precipitate. Ethyl uvitonate may be obtained by heating the potassium salt of the acid with alcoholic ethyl iodide at  $130^\circ$ ; it is insoluble in dilute ammonia, soluble in hydrochloric acid. When heated rapidly, it can be distilled in small quantity, but is decomposed by continued heating. A. K. M.

**Condensation to Pyridine-derivatives.** By C. BÖTTINGER (*Ber.*, 17, 53—54).—The author refers to a previous paper (*Annalen*,

208, 122) in which he showed that the formation of uvitonic acid from pyruvic acid is only possible by the separation of hydrogen, which, however, does not become free, but reduces a portion of the pyruvic acid. The author has made many experiments with the view to avoid this loss of pyruvic acid, and to improve the yield of uvitonic acid. On treating ammonium imidopyruvate with bromine-vapour, a violent reaction takes place with evolution of carbonic anhydride. When the bromine is in excess uvitonic acid separates as a pale-yellow powder, which becomes colourless when washed, whilst the liquid contains formic acid, bromoform, and probably bromine-derivatives of aldehyde. The formation of these compounds shows that only a portion of the pyruvic acid has been converted into uvitonic acid.

A. K. M.

**Synthesis of Anthraquinoline.** By C. GRAEBE (*Ber.*, 17, 170—171).—By heating anthramine with nitrobenzene, glycerol, and sulphuric acid the author has obtained anthraquinoline. This substance is identical with that previously prepared by him by heating alizarin-blue with zinc-dust (*Abstr.*, 1880, 262), thus further confirming the accuracy of the constitution—



assigned to anthraquinoline.

A. J. G.

**Bases of the Pyridine and Piperidine Series.** By A. LADENBURG (*Compt. rend.*, 98, 516—518).—The bases of the pyridine series are tertiary bases, and they combine with alcoholic iodides forming quaternary iodides. When these iodides are heated in sealed tubes at about 290°, they are partially converted into hydriodides of tertiary bases homologous with the pyridine employed. By this reaction, two isomeric bases are always obtained: one, which is formed in largest proportion, belonging to the  $\gamma$ -series, whilst the other, obtained in smaller quantity and having a higher boiling point, probably belongs to the  $\alpha$ -series.

When the compound of pyridine with ethyl iodide is treated in this way, it yields two lutidines, one of which boils between 153° and 154°, and yields isonicotianic acid on oxidation, whilst the other boils at about 166°, and on oxidation yields traces only of an acid which has not yet been isolated. The compound with propyl iodide yields two collidines, one of which,  $\gamma$ -propyl-pyridine, boils at 163°, and yields isonicotianic acid on oxidation, whilst the other boils at 174°, and is characterised by its slightly soluble and distinctly crystalline platino-chloride. The compound with methyl iodide seems to behave in a precisely similar manner, but the products have not yet been isolated. If these quaternary iodides are heated at a still higher temperature, ammonia and a considerable proportion of aromatic hydro-

carbons are formed. Ethylbenzene was obtained in this way from the compound with ethyl iodide.

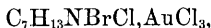
The conversion of pyridine bases into piperidine bases is effected by the action of sodium on a hot alcoholic solution, practically the theoretical yield being obtained, and in this way a whole series of homologues of piperidine can be prepared. Pyridine yields a piperidine, which seems to be identical with the piperidine obtained from piperine. Crude methyl-pyridine from Dippel's oil, however, yields a methyl-piperidine entirely different from that described by Hofmann. It is a transparent, strongly alkaline liquid, which boils at  $122^{\circ}$ , and has the odour of piperidine. It dissolves in water with development of heat, but separates from a very strong solution on heating. It yields a crystalline and non-deliquescent hydrochloride, a very soluble crystalline platinochloride, and a much less soluble aurochloride, which melts in slightly warm water. The crude methyl-pyridine from which this base was obtained contained  $\beta$ -methyl-pyridine, together with a larger proportion of  $\alpha$ -picoline.

$\gamma$ -Ethylpiperidine is obtained in the same way from the  $\gamma$ -ethylpyridine prepared by the method described above. It boils at  $143^{\circ}$ , forms a crystalline hydrochloride, has an odour resembling that of conicine, and behaves like this latter compound in contact with water.

C. H. B.

**Piperethylalkine Bromide.** By A. LADENBURG (*Ber.*, 17, 154—155).—The hydrobromide of piperethylalkine is heated with 1 mol. bromine in sealed tubes for six hours, first at  $100^{\circ}$ , then at  $120^{\circ}$ : the solid product is evaporated several times with water to remove hydrobromic acid, and finally crystallised from absolute alcohol.

*Piperethylalkine bromide*,  $C_7H_{13}NBr_2$ , so obtained crystallises in brilliant, colourless, thin prisms; it is sparingly soluble in alcohol, very readily in hot water. It can be regarded as the hydrobromide of *bromovinylpiperidine*,  $C_5H_{10}:N(HBr)C_2H_2Br$ . Treated with silver chloride, it yields the corresponding *hydrochloride*,  $C_{17}H_{13}NBrCl$ , forming colourless needles; the *platinochloride*,  $(C_{17}H_{13}NBrCl)_2 \cdot PtCl_4$ , crystallises in orange-coloured prisms; the *aurochloride*,



forms needles, which are sparingly soluble and melt in hot water. By treating it with silver oxide, all the bromine is removed from piperethylalkine bromide; several bodies are produced, but these have not as yet been separated. By treatment with sodium-amalgam, the bromide is converted into ethylpiperidine and ethenylpiperidylamine, the reaction being represented by the equations  $C_5H_{10}:N.C_2H_2Br + 2H_2 = NEtC_5H_{10} + HBr$  and  $2C_5H_{10}:N.C_2H_2Br + 3H_2 = N_2(C_5H_{10})_2C_2H_4 + 2HBr + C_2H_4$ .

A. J. G.

**Synthesis of Piperidine.** By A. LADENBURG (*Ber.*, 17, 156).—Pyridine cannot be converted into piperidine by the action of tin and hydrochloric acid, but by the action of sodium on an alcoholic solution of pyridine the hydrogenisation can be effected, although only in small part. The separation of the bases was effected by nitrous acid, the resulting nitrosopiperidine being afterwards decomposed by



hydrochloric acid. The platinochloride prepared from the base showed a complete agreement in properties with those of piperidine platinochloride.

A. J. G.

**Methyltropidine.** By C. F. ROTH (*Ber.*, **17**, 157—159).—*Methyltropidine* is obtained by the action of freshly precipitated silver oxide on an aqueous solution of tropidine methiodide. It is a colourless syrupy oil of distinctly tropylene-like odour; cannot be distilled without decomposition; it is soluble in ether and chloroform. The *platinochloride*,  $(C_9H_{15}N)_2, H_2PtCl_6$ , crystallises well, and is readily soluble in water; it melts at  $120^\circ$ . The *picrate*,  $C_9H_{15}N, C_6H_2(NO_2)_3.OH$ , crystallises from hot water in golden-yellow silky plates. The *hydrobromide*,  $C_9H_{15}N.HBr$ , forms brilliant colourless crystals.

A. J. G.

**Belladonine.** By A. LADENBURG and C. F. ROTH (*Ber.*, **17**, 152—153).—When this alkaloïd or mixture of alkaloids is boiled with alkalis, it readily dissolves, and is decomposed into tropine and an *oxytropine*, which gives a platinochloride,  $(C_8H_{15}NO_2)_2, H_2PtCl_6$ , crystallising in large red quadratic prisms, readily soluble in water; the acids formed at the same time are tropic acid, and its decomposition-products, atropic and isatropic acids. It is therefore possible that "belladonine" is a mixture of atropine and oxyatropine,  $C_{17}H_{23}NO_4$ ; further investigations are in progress.

A. J. G.

**Hyoscine.** By A. LADENBURG and C. F. ROTH (*Ber.*, **17**, 151—152).—Ladenburg has shown that on boiling hyoscine with alkalis or baryta, it is resolved into tropic acid and pseudotropine, a base isomeric with tropine (*Abstr.*, 1881, 56). *Pseudotropine* crystallises in rhombohedrons, melts at  $106^\circ$ , and boils at  $241$ — $243^\circ$  (tropine crystallises in the rhombic system, and melts at  $62^\circ$ ); it is less hygroscopic than tropine, is very readily soluble in water, readily soluble in chloroform, sparingly in ether. Its aurochloride melts at  $198^\circ$ . By the action of methyl iodide on an aqueous solution of pseudotropine at  $106^\circ$ , *pseudotropine methiodide*,  $C_8H_{15}N.MeI$ , is obtained in colourless rhombohedrons, readily converted into the periodide by iodine. By shaking the iodide with freshly precipitated silver chloride, and adding platinic chloride to the solution, the platinochloride,  $(C_{19}H_{18}N)_2, H_2PtCl_6$ , is obtained in fine brilliant reddish-yellow plates. Proof of the identity of the tropic acid from hyoscine with that from other sources was obtained by its conversion into atropine when treated with tropine and hydrochloric acid.

A. J. G.

## Physiological Chemistry.

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**Milk.** By E. DUCLAUX (*Compt. rend.*, **98**, 438—441, and 526—528).—The albuminoid matter in milk may be divided into *colloidal casein*, *casein in suspension*, and *soluble casein*, the latter being capable of passing through biscuit earthenware. Small battery cells give good results, but the larger cells do not yield a filtrate of constant composition, even from the same milk, in consequence of inequalities in the earthenware. This method of filtration separates those substances which are in suspension, *i.e.*, fat, casein, &c., from those which are in solution, *i.e.*, sugar, inorganic salts, &c. The original milk and the filtrates were examined by the methods described in the author's memoir (*Ann. de l'Institut Agronomique*, 1879—1880). The following results were obtained with a sample of Cantal milk:—

	In suspension.	In solution.
Fat.....	3·32	—
Sugar.....	—	4·98
Casein .....	3·31	0·84
Calcium phosphate ....	0·22	0·14
Inorganic salts.....	—	0·39
	<hr/> 6·75	<hr/> 6·35

In this case, the soluble casein is about one-fifth of the total casein, but the proportion is rarely so high: in Cantal milk, the amount of soluble casein varies between 4 and 6 grams per litre; this proportion remains approximately constant, and does not sensibly change, even when the milk is kept for a considerable time. It is only slightly affected by the action of heat; the filtrate becomes turbid on boiling, but the precipitate is very slight, and gradually redissolves. The action of heat on the other two varieties of casein causes them to agglomerate, and the deposit inside the porous cell after filtration is always more compact if the milk has been boiled. Slight acidity causes a portion of the colloidal casein to pass into the suspended condition, and slight alkalinity converts some of the suspended casein into the colloidal form, but neither of these conditions has any effect on the soluble casein. The proportion of soluble casein in normal milk is not only approximately constant, but seems to be independent of the nature of the milk, and is sensibly the same in the milk of cows from various districts, in goats', asses', and human milk. The proportion of soluble casein is increased to a slight extent by the addition of water, and to a much greater extent by the presence of the diastase to which the author has previously given the name *casease*. In one case the proportion of soluble casein was 0·61 per cent., but under the influence of casease it increased in 8 hours to 1·80, and in 24 hours to 2·20 per cent., after which it remained constant, one-third of the total casein being still in the colloidal condition. The destruction of the equilibrium thus established required a very much longer time, or

the addition of a further quantity of casease. The casein can be more quickly converted into the soluble form by addition of some of those microbes which produce casease (*loc. cit.*), and which continually secrete this substance, whilst at the same time they use up the casein already existing in the soluble form for their own nourishment. The secretion of the casease is in fact the means by which these microbes prepare their own food at the expense of the suspended and colloidal casein, and is strictly analogous to the action of the pancreatic juice in the higher animals.

Hammarsten supposed that the action of rennet on milk is to split up the casein into two new albuminoids, one of which is insoluble in presence of the calcium phosphate contained in the milk, and carries down a portion of this phosphate with it, whilst the other, corresponding to lacto-protein, and called *whey-protein* by Hammarsten, remains in solution. The author treated milk with rennet free from casease, care being taken to prevent the access of bacteria as far as possible, and examined the resulting liquid by the filtration method. The results of one out of a number of experiments are given in the following table:—

	In suspension.		In solution.	
	Milk	Whey.	Milk.	Whey.
Fat .....	4.30	0.85	—	—
Sugar .....	—	—	5.37	5.73
Casein .....	3.53	0.46	0.37	0.36
Calcium phosphate..	0.23	—	0.17	0.17
Inorganic salts ....	—	—	0.40	0.43
	8.06	1.31	6.31	6.69

The proportion of soluble casein and of dissolved calcium phosphate is the same in both the milk and the whey. The suspended calcium phosphate is, however, carried down together with the fat and the casein in the curd. Hammarsten's supposition is, therefore, not confirmed by experiment, since the amount of soluble casein is not increased, and the calcium phosphate plays no active part in the formation of the curd.

From the above table, it appears that 0.46 of the colloidal casein has not been converted into the solid form, and it is found that the whole of the coagulable casein is never precipitated, although the amount remaining in solution diminishes if the proportion of rennet is increased. Milk may be regarded as a system in which the three forms of casein are in equilibrium, this equilibrium being disturbed by the addition of minute quantities of inorganic salts, ferments, &c. Coagulation corresponds to the slow and regular production in a liquid mass of a state of equilibrium which requires the solidification of a dissolved substance, but there is no evidence to show why part of the casein should be precipitated in presence of rennet. The explanation is not to be sought in any specific properties of rennet, for other substances produce the same effect, nor in the specific properties of casein, since other bodies, such as oxide of iron, can exist in the same three

states. Coagulation, in fact, appears to be simply a problem in molecular mechanics which cannot be solved in the present state of our knowledge.

C. H. B.

**Observation on a Note by Calmels "On the Poison of Batrachians."** By A. GAUTIER and ÉTARD (*Compt. rend.*, **98**, 631).—Calmels stated (*Compt. rend.*, **98**, 536) that the carbylamines are produced by the splitting up of the isocyanacetic acid and its homologues which pre-exist in the poison, and he considers that these same carbylamines must be present amongst the products of putrefaction, and be closely related to the ptomaines. The authors have observed the presence of carbylamines amongst the products of the bacterial fermentation of albuminoids, more especially in the chloroform extract which contains the ptomaines (this vol., 89).

C. H. B.

**Poisons and Drugs which Act on Hæmoglobin, especially those which convert it into Met-hæmoglobin.** By G. HAYEM (*Compt. rend.*, **98**, 580—583).—Dissolved hæmoglobin is much more sensitive to the action of substances, such as amyl nitrite, potassium ferricyanide, and sodium nitrite, which can convert it into met-hæmoglobin, than is the hæmoglobin existing in blood corpuscles, and when once the former has been converted into met-hæmoglobin, it remains in that condition, whereas the latter after some time resumes its original condition and properties. Substances which, like amyl nitrite in moderate doses, do not destroy the corpuscles, do not produce any sensible anæmia, whilst those which have that effect, *e.g.*, sodium nitrite, cause somewhat rapid anæmia. The resistance which the hæmoglobin in the corpuscles offers to the action of substances which tend to convert it into met-hæmoglobin explains why these substances can be introduced into the blood even in considerable quantity without producing any sensible effect on it. This resistance is assisted by the rapid elimination of these substances, and by the changes which some of them, *e.g.*, ferricyanides, rapidly undergo in the organism.

C. H. B.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Influence of Salicylic Acid on Alcoholic Fermentation.** By G. HEINZELMANN (*Bied. Centr.*, 1883, 503).—The author's experiments show that the vitality of yeast is completely destroyed by the presence of 0.15 gram of salicylic acid per 400 c.c. of sugar solution, whilst the addition of 0.01 per cent. favours its greatest activity, and although the yeast plant does not propagate, nevertheless the cells developed in the presence of salicylic acid are stronger and larger than those produced in a solution free from that acid. Moreover under similar circumstances the production of alcohol in a given time is greater.

The addition of 0·1 gram of salicylic acid per litre of "mashing" favours fermentation, especially with pure sugar solutions.

D. A. L.

**Bacillus Butylicus.** By FITZ (*Bied. Centr.*, 1883, 503).—This bacillus is capable of yielding other products of fermentation than butyric acid. In the author's experiments, the following results were obtained :—

Product of fermentation.	100 glycerol.	100 mannitol.	100 invert-sugar.
Butyl alcohol.....	8·1	10·2	0·5
Butyric acid .....	17·4	35·4	42·5
Lactic acid .....	1·7	0·4	0·3
Succinic acid .....	—	0·01	trace
Trimethylene alcohol .....	3·4	—	—

Milk-sugar is not attacked.

D. A. L.

**Chemistry of Plants.** By M. BALLO (*Ber.*, 17, 6—12).—The author previously showed that in aqueous solutions of carbonic anhydride, the latter exists as hydroxide (*Abstr.*, 1883, 574), and he concludes therefore that this is the form in which it becomes assimilated by plants. He finds that the reduction of carbonic anhydride to formic acid can be effected not only by the action of potassium on the moist gas, but also by the action of an energetic reducing agent (sodium-amalgam) on alkaline hydrogen carbonates, and on calcium hydrogen carbonates, this being of interest in connection with plant chemistry through the wide distribution of the latter salt in water. Glycollic acid, which has been shown to occur in unripe grapes, and also tartaric acid have been obtained by the reduction of oxalic acid (*Bull. Soc. Chim.*, 27, 3; *Annalen*, 166, 124). Tartaric acid has likewise been shown by Liebig and others to be an oxidation-product of most of the carbohydrates, and by reversing the process (*i.e.*, by reduction) it might therefore be better suited to the formation of these substances than carbonic acid. Whilst a portion of the oxalic acid of plants serves to decompose calcium sulphate, by far the greater portion must give rise to the production of glycollic and tartaric, or of malic and succinic acids. The conversion of formic acid (which is assumed to be the first reduction-product of carbonic acid) into oxalic acid in plants, is probably brought about by nitric acid; it is found that nitric acid does effect this conversion if the reaction be stopped when red fumes begin to be evolved. The author believes that this is the reason why nitrogen must be presented to plants in the form of nitrates; a portion of this is no doubt reduced to ammonia, a second portion probably to nitrous acid, whilst the greater part is reduced to nitric oxide, which, by the action of oxygen and water, becomes reconverted into nitric acid.

The reduction of oxalic to tartaric acid may be assumed to be effected by the coalition of two oxalic acid molecules or of one molecule oxalic acid with one molecule glycollic acid; whilst the production of acids containing an uneven number of CH.OH-groups can be explained by formic acid taking part in the reaction. By the further

reduction of the acids, alcohols are produced. It is not yet understood in what way the salts act in the vegetable and animal organisms, but the author thinks it possible that they assist in bringing about the formation of the more complicated products.

By the action of sodium on an ethereal solution of chlorhydrin, a hexyl alcohol,  $C_6H_{10}(OH)_4$  (*glycerythrol*), is obtained, homologous with erythrol. It is soluble in water and alcohol, insoluble in ether, and forms a thick yellowish syrup of bitter taste. A. K. M.

**Action of Rain, Dew, and Watering on Plants.** By J. WIESSNER (*Bied. Centr.*, 1883, 471—472).—The moistened leaves of plants transpire more freely than when they are dry, consequently a larger quantity of water is withdrawn from the soil by the roots; if then there is plenty of moisture in the ground, the plant flourishes, but if otherwise it drops and languishes. Plants should not be watered on the leaf unless the soil is likewise moist. The small amount of extra transpiration induced by dew can do no harm, as it is almost certain that the ground will be sufficiently moist to supply the requisite amount of water. The action of rain is more beneficial still, for then the supply of plant food is most rapid. E. W. P.

**Studies on Ripe Cherries and Currants.** By C. AMTHOR (*Bied. Centr.*, 1883, 499—500).—The following conclusions are deduced from numerous determinations. Some of the experiments lasted six weeks, terminating with the maturity of the fruit under investigation. With cherries, both water and dry matter showed a constant increase throughout the period of experiment, and at the termination the water amounted to 398, and the dry matter to 295 per cent. of the original. The rate of increase of these matters is not, however, always in the same proportion; for instance, four weeks previous to ripening, the increase in water is behind that of the dry matter, but afterwards matters are reversed. In ripe cherries, the ash increases 204 per cent., the phosphoric acid 195 per cent., therefore these constituents do not increase to the same extent as the dry matter and water, and consequently appear to suffer diminution when compared with the latter. Ripe kernels contained 19.1 per cent. ash, and 20 per cent. phosphoric acid; thus showing an increase in both constituents. As currants ripen, various constituents increase in quantity; during the six weeks of experiment, both water and dry matter increased by 62 per cent., whilst the percentage of ash in some berries rose by 50, of phosphoric acid by 47, and of sulphuric acid by 126 per cent. D. A. L.

**Distribution of Sugar in Beet, and the Position in the Beet of the Mean Amount of Sugar.** By G. MAREK (*Bied. Centr.*, 1883, 480—482).—For the determination of absolute weight, dressed roots were divided from top to root-end into eight cross-sections, but to study the distribution of sugar, the beets were cut lengthwise into halves, one set being employed for the determination of sugar in the various cross-sections, from top to root-end, whilst in the other set similar determinations were made in peripheric zones from the centre to the

outside. With regard to the absolute weight, the uppermost portion contains 30·87, the lowest, or tail or root-end, 1·33 per cent. of the entire weight of the root (comp. Abstr., 1883, 124, and this vol., 356). The amount of juice obtained from each separate part is in the same relation. The sap of highest sp. gr. is found in the second and third eighth from top, then follows the first, and finally the others in succession, the sp. gr. diminishing towards the root-end. The rotatory power is greatest in the second section from the top, then sinks as the sections get nearer the root-end; that of the top section lies between five and six. For the determination of lateral distribution, the upper portions (from the neck of the root) only were employed, and these were carefully divided into seven semicircular pieces. The absolute weight increases from centre to the outside, the centre being lighter. Sp. gr., amount of sugar, and purity coefficient are comparatively low in the centre portions, then increase to the sixth part, and are lowest in the exterior layer. The position of the mean amount of sugar lies between the first and second eighth in large and medium beets, but is somewhat higher in small roots.

D. A. L.

**Effect of Drying, of Remoistening Dry Beets, of Frost, and of Winter Storage on the Constitution of Sugar-beet.** By G. MAREK (*Bied. Centr.*, 1883, 484—487).—The first series of experiments were made to determine if the loss of water could be made up and polarisation readjusted by the addition of moisture to dry tested beets. Loss of water occasions concentration of the sap, and therefore more or less noteworthy changes in the polarisation and purity. The loss of water is greatest during the first two days' exposure of the roots, the quantity varying greatly with the prevalent temperature and the mode of covering the roots. When the loss of water is small, it can be restored by simply wrapping the roots in a damp cloth, or sprinkling them with water. When, however, the loss is great, it cannot be renewed in that manner. The most effectual way of compensating for evaporation is to lay the roots in soak, which method is of doubtful practical utility on account of its effect on the soundness of the root.

The cells of thawed frozen roots are clear and transparent, whilst the sap is difficult to filter, and very prone to mucous fermentation. It contains a calcium salt, which is not decomposed by carbonic anhydride; these defects of the thawed sap cannot be rectified by mixing with good extract. Roots may freeze when they are in the ground, or when they lie uncovered, or insufficiently covered on the ground, or during transport. The first case rarely happens, as the beet can withstand  $-7^{\circ}$  without freezing, provided it remains undisturbed, it is therefore advisable not to pull roots while the ground is frozen. The second case can be prevented by covering them with a sufficiently thick layer of earth. Roots frozen during transport should be used at once. In order to ascertain the time of the initial change in the internal composition of frozen roots, the author proceeded as follows:—20 beets were each divided into 8 equal parts, and subjected to experiments in different stages: (1), fresh; (2), after 24 hours at  $-3^{\circ}$ ; (3), after 48 hours at from  $-3^{\circ}$  to  $-4^{\circ}$ ; (4), after 5 days' storage of the



frozen beet at 5°; (5), after 14 days; (6), after 30 days' storage. The sap testings were as follows:—

Stages.	Sp. gr.	Per cent.			
		Dry matter.	Polarisation.	Not sugar.	Purity.
1	1·0630	15·371	13·429	1·942	88·36
2	1·0650	15·837	13·109	2·728	82·77
3	1·0810	19·497	16·518	3·979	84·72
4	1·0650	15·837	13·725	2·112	86·66
5	1·0645	15·721	13·860	1·861	88·16
6	1·0585	14·309	9·690	4·619	67·71

The decomposition which interferes with the manufacturing processes commences about 20 days after freezing.

From another series of investigations, the author shows that the spontaneous changes of beet which take place during the winter were variable during the seasons 1880-81 and 1881-82, and therefore the exact period at which the greatest amount of sugar is to be found has not been definitely fixed. Thus the diminution in sugar from December, 1880, to March, 1881, was 4·44 per cent.; whilst from November, 1881, to February, 1882, it was 2·691 per cent. The loss of sugar commenced in 1880-81 in January, in 1881-82 in December.

D. A. L.

#### Poisonous Action of Ammonium Thiocyanate on Plant Life.

By M. MÄRCKER (*Bied. Centr.*, 1883, 497).—Experiments prove that superphosphate may be mixed with 1 per cent. of ammonium thiocyanate without injurious effect; whilst with oats as much as 100 kilos. of this salt per hectare does not act prejudicially (comp. Abstr., 1883, 495-496).

D. A. L.

**Influence of Thick and Thin Sowing, and of the Manuring on the Yield of Oats.** By O. BESSLER and M. MÄRCKER (*Bied. Centr.*, 1883, 472-488).—The quantity of seed sown was 22 lbs. per morgen, distance 23·5 cm. between the drills, and 38 lbs. distance 17 cm. In the former case, even with the assistance of manures, the yield obtained did not reach that of the 38 lbs. per morgen. Addition of phosphate produced no great increase, but advantage was gained by the use of Chili saltpetre, and then the increase was proportional to the increase of nitrogen; with small quantities of nitrate, the addition of phosphates was productive of good results, but this was not so when much nitrate was used. These manures equally raised the yield of grain and straw, which were in the ratio of 1 : 1·3 with thick sowing, and 1 : 1·22 with thin sowing. Plants growing closely together were poorer in albuminoids than those at a greater distance apart, and the presence of extra phosphates did not raise the percentage of these compounds; neither did nitrogen manures in addition to phosphates. Seeing that the higher the yield was, the higher was the percentage of

albuminoid matter, the conclusion is drawn that the larger the crop the better is its quality, and that moderate manuring renders a crop better in quantity and in quality. E. W. P.

**Cultivation of Peruvian Rice (*Chenopodium Quinoa*) in Austria.** By E. v. RODICZKY (*Bied. Centr.*, 1883, 487—488).—The author has conducted some successful experiments in this direction in Hungarian Altenburg during the seasons 1879 and 1882. Sowing on 16th March in a loamy soil poor in humus, the plants appeared on the 26th; on 1st June they were hoed, they flowered at the commencement of July, and were ripe for harvest in the middle of September; in another case the sowing was on 5th April, the plants came up on 20th, were in flower on 12th July, but on account of unfavourable weather did not ripen until the middle of October. 7—9 kilos. of seed were sown per hectare in rows 50—60 cm. apart, the crop was hoed once, and at a later date thinned to stand 25 to 30 cm. apart in the rows. The yield is very good, 17 grams (even 87 grams) per plant, 2700 kilos. per hectare. The percentage composition of the grain, according to Voelker, is as follows:—Dry matter 83·90, starch 58·22, extractive matter 5·12, fat 4·81, albuminoids 11·71, ash 4·25. It is a very hardy plant, withstanding both frosts and drought. In Peru, it is eaten green as a vegetable, whilst the grain is used in soups, &c., like sago. It does not appear to be fitted for fodder, but as it produces an abundance of leaf and stem, the author considers it adapted for green manuring. D. A. L.

**Cultivation of *Vicia villosa* and of *Pisum arvense*.** By MÄRCKER and others (*Bied. Centr.*, 1883, 488—491).—The *Vicia* is best sown as soon as the ground is free from frost, in March, using 10 kilos. of vetch and 20 kilos. of summer rye per morgen. It is advisable to harvest when the rye is ripe, then the partially ripe vetch dries easily without losing its vitality. Perfectly ripe vetch does not scatter, unless it is bound and carried in hot dry weather, when the seed pods break off, and are left in the field. Dry soil of Class 7 or 8, as free from weeds as possible, is the most suitable for this plant; it thrives, however, on deep moist soils, but does not produce much seed, it is therefore advisable to feed off with sheep in such cases.

On poor land the following rotation is recommended:—(1), Potatoes (manured); (2), *Vicia villosa* (sand vetch), with summer rye; (3), winter rye. Kainite and phosphate are probably favourable manures. For better wheat and root land the following: 1, Roots or potatoes manured; 2, barley, half with clover; 3, half clover, *V. villosa* as fodder; 4, wheat. *V. villosa* is winter-proof, therefore for early green fodder it may be sown in the autumn along with winter rye or else a mixture of oats, and this vetch may be sown at intervals of three or four weeks, so that there will be green fodder always at hand until late in the autumn. To prevent the *V. villosa* becoming a permanent weed, the stubble should be pulled up twice, or it may be used as forerunner of manured potatoes in rotation.

Heinrich has cultivated *V. villosa* and *Pisum arvense* on light sandy soil, with marly subsoil in some places. Both varieties of seed were

mixed with one-third their weight of summer rye, and were dressed with 5 kilos. blood manure per plot of 2 ares. The yield of vetch was small, 26·7 centners of straw and 3·2 centners of grain per hectare. Peas yielded per hectare, on the land with marly subsoil, 69·5 centners straw, &c., 22·2 centners grain; on the other soil, straw, &c., 47·5 centners, and grain 15·4 centners.

Troschke has cultivated "white pea," "grey pea," and "sand pea" (*P. arvense*), in order to investigate and compare the relative composition at various stages of growth. The harvest results were lost owing to unfavourable weather; but the plants at the beginning of blossoming, and subsequently the ripe seed, have been submitted to chemical examination, with the following results; figures are per cent. :—

Constituent.	Plant at beginning of blossoming.			Ripe seed.		
	White pea.	Grey pea.	Sand pea.	White pea.	Grey pea.	Sand pea.
Water.....	16·0	16·0	16·0	16·0	16·7	16·2
Ash.....	6·9	7·8	7·2	2·6	3·8	4·1
Albuminoids...	22·7	21·9	20·8	23·3	22·7	21·4
Fibre.....	24·9	23·1	21·8	6·2	7·2	7·0
Extractive matter	26·8	28·7	30·8	50·2	47·8	49·5
Fat.....	2·7	2·5	3·4	1·7	1·8	1·8

Two samples of "sand" pea had the following composition per cent. :—

	Grain		Straw	
	From Gr. Warbelin.	From Melln.	From Gr. Warbelin.	From Melln.
Water ..	16·8	14·7	15·0	16·0
Ash ..	2·3	2·5	4·0	3·9
Albuminoids.....	21·8	23·3	7·3	6·8
Fibre.....	5·8	6·0	38·5	43·5
Extractive matter.....	51·8	52·1	33·6	28·7
Fat.....	1·5	1·4	1·6	1·1

It will be seen that in composition this variety of pea somewhat resembles other varieties; it, however, differs from the latter in yielding better harvest and economising the soil. Von Borecke has investigated the cultivation of this pea (*P. arvense*) on various soils, and has found sandy soil to be the most favourable. D. A. L.

**Composition of Silage.** By A. SMETHAM (*Jour. Roy. Agri. Soc.*, 1884, 380).—The silage from Tatton Park was made from fresh grass

mown in July; the grass was cut into chaff, and about 8 parts of salt added per 1000 of grass. The composition of the grass and of the resulting silage is given below. The silage from Wilmslow was made from grass mown in October; the grass was not chaffed, no salt was added. The silage from Hayton was made from chaffed clover and rye-grass mown early in September. The sample was taken for analysis in March.

	Tatton Park.				Wilm-slow.	Hayton.
	Original grass.	Silage from grass.			Silage from grass.	Silage from clover and rye-grass.
		1½ ft. to 2 ft. from bottom.	1 ft. to 1½ ft. from bottom.	Bottom layer.		
	In 100 parts of fresh substance.					
Water .....	70·48	68·74	65·84	78·65	81·38	78·10
	In 100 parts of dry substance.					
Insoluble albuminoïds ..	6·94	3·65	3·75	3·84	6·12	6·53
Soluble albuminoïds ....	3·06	6·08	6·06	5·90	7·09	5·20
Fat (ether extract) ....	2·80	7·52	5·39	4·31	3·98	6·66
Soluble carbohydrates ..	11·65	5·69	8·61	2·81	1·18	7·85
Digestible fibre .....	36·24	29·81	36·24	33·72	36·63	25·80
Indigestible fibre .....	32·33	31·67	26·64	34·42	31·10	36·76
Soluble mineral matter..	5·24	13·98	11·47	12·51	7·35	6·17
Insoluble mineral matter	1·74	1·60	1·84	2·49	6·55	5·03
Acidity as acetic acid ..	—	0·99	1·02	2·34	0·97	1·51

The central layer of silage from Tatton Park contained in the fresh state 0·34 per cent. of alcohol; in the bottom layer only a trace of alcohol was found. The amount of free acid increased greatly towards the bottom; the liquid occurring there contained 0·89 per cent. The acid is reckoned as acetic, but in fact includes both butyric and lactic. The marked increase in the quantity of ether extract is probably due to the presence of acids soluble in ether. The albuminoids are merely calculated from the nitrogen present. The soluble nitrogenous compounds were clearly not wholly albuminoid (see this Journal, Trans., 122), a part apparently were amines. The most considerable changes resulting from ensilage are apparently in the albuminoids, resulting in the formation of simpler soluble bodies, and in the soluble carbohydrates, which suffer loss by fermentation.

R. W.

**Changes which take Place in the Conversion of Hay into Silage.** By F. J. LLOYD (*Chem. News*, 49, 210).—Taking the analysis of grass, and of silage made from it at Tatton Park (see preceding abstract), the author finds that the proportion of nitrogen in dry organic matter in the two substances is as 100 : 106, and concludes that 106 of organic matter as grass have yielded 100 as silage. He then compares the composition of these two quantities, and concludes, in addition to the deductions given above, that there is no increase in the amount of digestible fibre during ensilage.

R. W.

**Heaping Potatoes.** By SCHLEH (*Bied. Centr.*, 1883, 483—484).—Experiments were made with “Red Heidelberg,” “Sieberhauser,” and Dabersche potatoes; heaping increased the total yield in the latter case only. In all cases it produced more large tubers, but did not prevent disease, and on the whole favoured extension of the stolons. In conclusion, the author considers heaping on dry sandy and light soils not only superfluous, but, under certain circumstances, even detrimental.

D. A. L.

**Digestibility of Wheat Chaff, and the Changes which it undergoes by different Methods of Preparation, &c.** By G. KÜHN and others (*Bied. Centr.*, 1883, 455—471).—As it was first necessary to determine the digestibility of the hay used for fodder in addition to the chaff, seven bullocks were put up and fed with three qualities of hay, both dry and moistened; afterwards they were fed with the hay to which was added chaff, dry, moistened, and boiled. Several tables show the result of these experiments, which may be summed up in the following sentences:—The digestibility of the hay is not affected by previous moistening with cold water or chaff tea; moistening of the hay has no influence on the digestibility of the chaff; steeping of chaff in cold water for 24 hours does not render either the chaff or the hay more easy of digestion; steeping the chaff renders its albuminoid matters less easy of digestion, and the less so the higher the temperature of the water, and the longer the time during which the steeping is conducted.

E. W. P.

**Amount of Easily Digestible Albuminoids in Germinated Maize.** By A. STUTZER (*Bied. Centr.*, 1883, 497).—Maize becomes less nutritious by germination, because the albuminoids are decomposed into substances of lower nutritious value than albumin. The germinated samples examined contained only a few tenths or even as little as 0.1 per cent. of easily digestible albuminoids.

D. A. L.

**Effect of High Farming on the Amount of Nutritious Matter in Straw.** By M. MÄRCKER (*Bied. Centr.*, 1883, 500).—Three years' experiments with oat-straw on the highly-cultivated soil of Saxony yielded unfavourable results, inasmuch as the straw frequently contained only 1 per cent. of albuminoids, whereas, according to Wolf's mean, it should amount to 4 per cent. It is for this reason that oat-straw is only of small value in Saxony. Other experiments with grain show that the amount of albuminoids diminishes with a

limited application of nitrogenous manures and *vice versâ*. For example, by the use of 2 centners of sodium nitrate and 1 centner of superphosphate,\* the amount of albuminoids in oat-grain was raised from 7 to 11 per cent. (compare Abstr., this vol., 630).

D. A. L.

**Fertility of a Soil which had been Removed from its Original Position and subsequently Replaced.** By M. MÄRCKER (*Bied. Centr.*, 1883, 496).—The soil in question was a surface soil rich in humus; it was removed (in order to work the underlying lignite) and subsequently replaced; after which operation it was lightly manured with artificial manures and sown with barley, when a luxuriant crop of straw was obtained. The author suggests the following explanation: that by removal the soil becomes looser, and moreover during removal, more thorough contact with the air ensued, and consequently there was a more energetic decomposition of nitrogenous matter, accompanied by nitrification. The detrimental effect of the large quantity of nitric acid thus produced could be avoided by the abundant use of phosphatic manures, whilst the consistency of the soil might be improved by a dressing of kainite and by mechanical means.

D. A. L.

**Fermentation of Manure.** By U. GAYON (*Compt. rend.*, 98, 528—530).—Fresh manure undergoes two entirely different kinds of fermentation, according as it is exposed to the air or is kept in a closed vessel. If exposed to the air, the temperature gradually rises until it attains a maximum of 74°, after which it gradually falls, because the mass has become much drier and ceases to oxidise. If, however, water is added, combustion recommences and the temperature again rises. The development of heat causes the evolution of large volumes of vapour, which carry off considerable quantities of ammonia. Microscopic examination shows that even in the most highly heated portions there are multitudes of torulæ, micrococci, bacilli, amœbæ, &c. Similar organisms have been observed in fermenting tobacco, even when the temperature has been as high as 80°.

If the manure is carefully protected from the air, there is at first a slight rise of temperature up to about 20°, due to absorption of the imprisoned oxygen, but afterwards the temperature gradually falls, until it is only one or two degrees above that of the surrounding air. Large quantities of carbonic anhydride and methane are given off, and the manure is found to be full of extremely minute anaerobic organisms, which can be cultivated in suitable fluids. When these cultivated organisms are brought in contact with cellulose, &c., carbonic anhydride and methane are given off.

C. H. B.

**Application of Artificial Manures in the Cultivation of Beetroot.** (*Dingl. polyt. J.*, 250, 553.)—According to Déhérain, ammonium sulphate has an injurious effect on the germination of

\* The extent of land is not mentioned; it is, however, most probably per morgen: 2 centners per morgen = 350 lbs. per acre.

beetroot when the soil does not contain a sufficient amount of organic matter. Ammonium sulphate reduces the yield of crop, whilst sodium nitrate diminishes the percentage of sugar. One hectare of unmanured soil yielded 46,600 kilos. roots with 16·24 per cent. sugar; after the addition of 1200 kilos. sodium nitrate, 57,400 kilos. roots with 9·97 per cent. sugar; and after treatment with 1200 kilos. ammonium sulphate, 37,200 kilos. with 13·38 per cent. sugar. Holdefleiss, on the other hand, recommends a judicious addition of farm-yard manure mixed with a small proportion of sodium nitrate. Farm-yard manure may be replaced by superphosphate and sodium nitrate. Too large a quantity of nitrogenous manures, however, impoverishes the soil.

D. B.

**Retrograde Phosphoric Acid.** By J. POST (*Bied. Centr.*, 1883, 448—449).—The superphosphate was examined at various periods; the acid estimated by means of aqueous ammonium citrate at 40° and at 90°. During the first two months as much soluble phosphoric acid was reduced as during the succeeding four; the amounts of ferric and aluminium phosphates, soluble in water, were also reduced by keeping, but a larger amount of these compounds became soluble in citrate at 40°; whilst but little difference was shown by citrate at 90°. The reduction must have been occasioned by combination of the originally free acid with some of the insoluble portions of the superphosphate, probably alumina or iron, forming calcio-aluminic or calcio-ferric phosphate.

E. W. P.

### Comparison of Dissolved and Undissolved Phosphates.

By B. DYER (*J. Roy. Agri. Soc.*, 1884, 113).—The first experiments were made at Horsham in 1882; the soil was a stiff clay containing no calcium carbonate. Swedes were grown with 5 cwt. per acre of coprolite superphosphate, and with 6½ cwt. (the same money value) of very finely-ground Cambridge coprolite. The comparison was made both with and without dung, but the produce obtained was not large; in each case the better result was from the undissolved phosphate. In the following year, oats were grown on the same plots without further addition of manure; the produce was again, on an average, better where the undissolved phosphate had been employed. The experiments with swedes were repeated in 1883. On this occasion, 235 bushels of lime per acre were ploughed in before sowing the crop. The same quantities of manure were applied as before. Owing to the dryness of the season, the crops were very small. The produce was in this instance distinctly better where the dissolved phosphate had been applied. These results confirm earlier experiments, showing that dissolved phosphates are more effective than undissolved when the soil contains lime. In the above experiments, the ground coprolite supplied more than twice as much phosphate as the superphosphate.

R. W.

**Manuring with Potash.** By F. FARSKY (*Bied. Centr.*, 1883, 457—459).—Pure salts of potassium reduce the yield of the crop, and the more the nearer the salt is to the seed. Potassium chloride is less lowering. The Stassfurt salts were distinctly harmful to barley and

rye, but the lowering effect is less the more moisture there is in the soil, which renders the solution of the salts dilute. Experiments with other crops showed that advantage was derived from the use of Stassfurt salt with most crops, excepting barley, oats, and, to some degree, rye and clover. Autumn manuring is better than spring.

E. W. P.

**Action of Sulphuric Acid as a Manure.** By F. FARSKY (*Bied. Centr.*, 1883, 447).—Strong sulphuric acid as well as sodium hydrogen sulphate in solution were applied to soil in boxes. The experiments were in duplicate, one set after the first moistening was not further wetted, but the other was kept moist with plain water.

The results were that the moistened sets brought no higher yield than a blank set, whilst the yields from the soils kept dry were lowered.

E. W. P.

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## Analytical Chemistry.

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**Apparatus for the Reduction of Measured Gas-volumes to Normal Condition.** By U. KREUSLER (*Ber.*, 17, 29—34).—The author describes two forms of apparatus, the principle of which is the same as in Vernon Harcourt's apparatus (*Abstr.*, 1883, 378).

A. K. M.

**The Alkaline Reaction of Glass as a Source of Error in Analysis.** By U. KREUSLER and O. HENZOLD (*Ber.*, 17, 34—40).—Whilst repeating Kjeldahl's experiments on the formation of ammonia by the action of sulphuric acid and potassium permanganate on organic compounds (this vol., 364), the authors made comparative experiments with pure ammonium salts, with the result that too high a percentage of ammonia was found. The same result was observed in blank experiments when no ammonia was present, the average alkalinity (estimated as ammonia) from three experiments being equal to 2.13 mgrms. nitrogen. The authors have traced this source of error to the decomposition of the glass employed in the experiments; they have also compared different sorts of glass, namely (1), readily fusible Thuringian glass; (2), less fusible Thuringian glass; (3), combustion tubing of very refractory Bohemian glass, and (4), more readily fusible Bohemian glass. Of these, the first is far the most readily attacked by water, the third being the least attacked, and yielding results which require no correction. The fourth is nearly as good as the third, whilst the second is much more readily acted on. The alkaline reaction of glass may be easily shown by boiling red litmus tincture in a test-tube, and by other such simple experiments.

A. K. M.

**Test for Available Chlorine in Bleach Works and Similar Establishments.** By R. BAUR (*Dingl. polyt. J.*, 251, 173—177).—The author considers that the simplest, quickest, and most accurate

method of determining the available chlorine in the baths of bleach works, paper works, &c., is Dupasquier and Bunsen's modified iodine method, a detailed account of which is given in the original paper.

D. B.

**Purification of Hydrogen Sulphide by Means of Hydrochloric Acid.** By W. LENZ (*Ber.*, 17, 209).—A reply to the criticisms of Otto (this vol., 638) on the method of purification of hydrogen sulphide from traces of arsenic as described by the author (this vol., 215).

A. J. G.

**Titration of Sulphurous Acid and its Salts.** By G. LUNGE (*Dingl. polyt. J.*, 250, 530—533).—Formerly it was assumed that an aqueous solution of sulphurous acid could be titrated with litmus exactly as the strong mineral acids are; that is, that the change of colour takes place when 2 mols. sodium hydroxide have been added to 1 mol. sulphurous acid. This, however, is not the case, as  $\text{NaHSO}_3$  is neutral to litmus. Litmus has been recently replaced in many cases by methyl-orange, which presents greater advantages for titrating carbonates or sulphides. The orange cannot, however, be employed with organic acids.

Thomson's experiments (*Chem. News*, 47, 136) having brought forward the important fact that the salts of sulphurous acid present have different kinds of neutrality towards indicators, the author repeated his experiments in order to confirm Thomson's results: in the course of this investigation, the author made a series of interesting experiments on the titration of bisulphites and of free sulphurous acid. He concludes that litmus and phenacetolin should be entirely rejected for the titration of sulphurous acid, for totally different results are obtained according as the change of colour is taken at a decided blue or a decided red. Methyl-orange, phenolphthalein, and rosolic acid are equally well serviceable; in the case of the orange, however, it must be noted that 1 mol.  $\text{SO}_2$  is saturated by 1 mol.  $\text{KHO}$ , and in the case of phenolphthalein and rosolic acid, by only half a molecule, *i.e.*, one equivalent of  $\text{SO}_2$  to one of  $\text{KOH}$ . A further confirmation of these results was obtained by some experiments with sulphites.

The novelty of the author's experiments is the abnormal behaviour of litmus and phenolphthalein.

D. B.

**Action of Soda Lime and Magnesia on the Salts of Ammonia and Organic Amines, and on the Titration of Aniline.** By G. LUNGE (*Dingl. polyt. J.*, 251, 36—41).—The author has made a series of experiments in order to ascertain which of the above-named three bases is the best adapted for liberating ammonia in analytical operations. The following conclusions were arrived at:—

1. Lime, magnesia, and soda in excess liberate all the ammonia contained in ammonium chloride equally well. The distillation should not, however, occupy much less than three hours, otherwise even lime or soda fail to expel all the ammonia.

2. In the presence of fatty (ethylamine) or aromatic amines (aniline), these are liberated under the same conditions as ammonia,

so that the assumption that magnesia avoids the decomposition of the organic amines originating in coal-tar and possibly contained in commercial ammonium salts, is erroneous, the employment of magnesia offers no advantage in respect of estimating the ammonia alone without the other amines. Quinoline was found to behave like aniline.

3. Lime and soda when distilled for three hours with an excess of ammonium chloride, liberate their full equivalent of ammonia; magnesia, however, on distilling for 3 to 5 hours, expels only about 85 per cent. of the theoretical quantity of ammonia (probably owing to the formation of a basic magnesium chloride difficult to decompose). Hence magnesium must always be employed in excess, whilst this is not necessary in the case of lime or soda.

Referring to the titration of aromatic amines, the author has found that methyl-orange when employed as indicator, is not changed by aniline salts, whilst aniline itself shows the reaction of a base. The same is the case with ortho- and para-toluidine, xylidine, meta- and para-phenylenediamine. Experiments have been made with these bases in the hope of being able to estimate the relative proportions of aniline and toluidine in commercial aniline oils, taking advantage of the difference of molecular weights, and although it was possible to titrate very small quantities of aniline mixed with ammonia salts with sufficient accuracy by methyl-orange, it was impossible to quantitatively estimate aniline along with toluidine in this way; owing to the fact that a slight difference in the test acid consumed (1 c.c. = 0.093 gram aniline or = 0.109 toluidine) will indicate a considerable difference in the proportion of the amines. D. B.

**Estimation of Lead as Lead Dioxide by Means of the Electric Current.** By F. TENNEY (*Amer. Chem. J.*, 5, 413—415).—Luckow, May and Riche have previously used this method. Using a solution of known strength of pure lead nitrate, very good results were obtained, when about 10 per cent. of nitric acid was added. A solution containing about 12 parts of copper to one of lead, allowed of an accurate separation and determination of the two metals, when from  $1\frac{1}{2}$  to 10 per cent. of nitric acid was present. In presence of iron the separation is also accurate. If large amounts of lead are present, either an aliquot portion must be taken, or a platinum dish may be made the positive pole and the dioxide washed by decantation. In the analysis of slags and mattes, the copper and lead are best precipitated by sulphuretted hydrogen, and the solution of the sulphides in nitric acid electrolysed. H. B.

**Qualitative Separation of Tin, Antimony, and Arsenic.** By E. BERGLUND (*Ber.*, 17, 95—98).—The solution of the sulphides in ammonium sulphide obtained in the usual way is acidulated with hydrochloric acid, the precipitate well washed, boiled with water, and sodium sulphide added. The solution is then boiled with copper oxide, when copper sulphide is formed and a colourless liquid obtained, containing sodium stannate, antimoniate, and arsenate; when cold, alcohol ( $\frac{1}{4}$ — $\frac{1}{3}$  vol.) is added to the filtrate, producing a white

precipitate containing the antimony. The filtrate is boiled to expel the alcohol, ammonium chloride added in excess, and then (whether a precipitate has been produced or not) a few drops of ammonia. Hydrogen sulphide is passed through the liquid, and if a precipitate forms, the passage of the gas is continued until the latter is dissolved. The arsenic is then thrown down as ammonium magnesium arsenate by the addition of ammonia ( $\frac{1}{3}$  vol.) and magnesia mixture, and the filtrate treated with hydrochloric acid, which precipitates the tin as stannic sulphide.

A. K. M.

**Testing Grape-sugar, and some Reactions of Sugars.** By WORM-MÜLLER and others (*Bied. Centr.*, 1883, 492—495).—A great many of the publications referred to in this memoir have already appeared in this Journal (*Abstr.*, 1883, 38, 624, 829, 1176; 1884, 502). Pure dextrose has been prepared from cane-sugar in the following way:—About 300 grams of finely powdered cane-sugar are mixed gradually in course of some weeks with 600 c.c. of 80 per cent. alcohol and 20 c.c. of fuming hydrochloric acid. The sugar dissolves, and after some time dextrose separates in beautiful white crystals, which are washed with alcohol and dried at 100°; they are easily recrystallised either from methyl or absolute ethyl alcohol. 50 per cent. of the raw sugar is converted in this manner. The description of Vivien's method (this vol., 502) is not quite accurate. The solution of 10 grams of sugar in 200 c.c. of water is mixed with diluted Fehling's solution of various strengths of which 10 c.c. represent respectively 0.01, 0.009, and 0.001 gram of glucose. To determine the amount of starch-sugar in sugar cane, Geissler makes use of the powerful reducing action which the former exerts on Fehling's solution, whereas the latter is inactive until "inverted." Starch-sugar has been detected in a commercial raspberry-juice.

D. A. L.

**Salicylic Acid in Beer and Wine.** By J. A. BARRAL (*Bied. Centr.*, 1883, 495—496).—In two series, each of three experiments, Ladureau employed (1) beer alone, and beer mixed respectively with (2) 4 and (3) 8 grams of salicylic acid per hectolitre. The three beers were exposed to the air (during spring in one case, and in the second series during summer) for two weeks and subsequently closed up for a month, after which period they were examined:—beer (1) was very sour; beer (2) only slightly; beer (3) not at all. To complete the investigation, the salicylated beer was employed for dietetic purposes for several weeks without any deleterious effect on the health of the experimenter. Therefore the addition, at most, of 10 grams of salicylic acid per hectolitre preserves the beer without affecting its use as a beverage. 50 to 80 milligrams of salicylic acid per litre is sufficient to prevent wine turning sour. The author therefore defends the use of salicylic acid, and maintains that a prejudicial amount would never be added owing to the facility with which salicylic acid may be accurately estimated.

D. A. L.

**Method of Testing Butter for Foreign Fats.** By H. BECKURTS (*Dingl. polyt. J.*, 251, 240).—The author has tested butter in accord-

ance with Reichert's method. 2·5 grams of the dried fat were saponified with 1 gram of potassium hydroxide and 20 grams of 80 per cent. alcohol. The mixture was heated on a water-bath to expel the alcohol; it was then diluted with 50 c.c. of water, and, as soon as the soap had dissolved, 20 c.c. of dilute sulphuric acid (1 acid to 10 vols.) were poured in and the mixture distilled, a platinum spiral being introduced to avoid bumping. The distillation was continued until exactly 50 c.c. were obtained. In the case of genuine butter, Reichert found that 14 c.c. of decinormal soda-solution were required to neutralise the distillate, but the author had to employ from 15·6 to 17·5 c.c., and concludes therefore that Reichert's numbers were too low. He also states that in order to obtain concordant results it is necessary to adhere strictly to the above proportions. D. B.

**Analysis of Beeswax.** By O. HEHNER (*Dingl. polyt. J.*, 251, 168—170).—The author dissolves 3 to 5 grams of beeswax in about 50 c.c. of methyl alcohol and titrates the cerotic acid with phenolphthaleïn and a solution of alcoholic potash, 1 c.c. corresponding with 0·3—0·4 c.c. of normal sulphuric acid. Having added potash in excess, the myricin is saponified and calculated from the quantity of potash required for the complete saponification, assuming that 1 c.c. normal alkali neutralises 0·41 gram cerotic acid and decomposes 0·676 gram myricin. The author obtained the following results:—

English wax from—

	Cerotic acid.	Myricin.	Total.
Hertfordshire.....	14·35	88·55	102·90
„ .....	14·86	85·95	100·81
Surrey.....	13·22	86·02	99·24
Lincolnshire .....	13·56	88·16	101·72
Buckingham .....	14·64	87·10	101·74
Hertfordshire.....	15·02	88·83	103·85
New Forest .....	14·92	89·87	104·79
Lincolnshire .....	15·49	92·08	107·57
Buckingham .....	15·71	89·02	104·73
Eight samples from merchants .....	13·12—15·91	86·73—89·58	99·85—105·49

Other kinds of wax from—

America .....	15·16	88·09	103·25
Madagascar .....	13·56	88·11	101·67
Mauritius .....	13·04	88·28	101·32
„ .....	12·17	95·68	107·85
„ .....	13·72	96·02	109·74
Jamaica .....	13·49	85·12	98·61
„ .....	14·30	85·78	100·08
Mogadore .....	13·44	89·00	102·44
Melbourne .....	13·92	89·24	103·16
„ .....	13·18	87·47	100·65
Sydney .....	13·06	92·79	105·85
„ .....	13·16	88·62	101·78

The English wax contained an average of 14·4 per cent. cerotic acid and 88·09 per cent. myricin. The foreign kinds were mostly coloured, and some had been adulterated with fat. The organic adulterants are either acids, palmitic or stearic acid; inert or saponifiable substances, stearin, palmitin, Japanese wax, spermaceti and carnauba wax; or substances which are not acted on by alcoholic potassium hydroxide, paraffin. 1 part stearic acid = 1·443 cerotic acid; 1 part palmitic acid = 1·601 cerotic acid, whilst 1·518 of the latter is equal to 1 of a mixture of these fatty acids. 1 part of a mixture of palmitin and stearin is equal to 2·391 myricin. Japan wax contained 6·21 per cent. palmitic acid and 94·12 per cent. palmitin. Spermaceti being as costly as beeswax is sometimes used as a substitute. Carnauba wax yielded 6·09 per cent. cerotic acid and 92·18 per cent. myricin. It is added to beeswax when the latter has been treated with fat. When paraffin is employed, the percentage of acid and saponifiable matter is reduced in proportion to the quantity of paraffin present, and can be calculated by difference unless other adulterants have been used, in which case it is necessary to determine the paraffin. If A is the percentage of free acid calculated as cerotic acid, and B the unsaponifiable substances calculated as myricin, we obtain the following equation, assuming  $x$  to represent the unknown quantity of cerotic acid,  $y$  that of the fatty acids,  $z$  of myricin, and  $w$  of the remaining substances:— $x = 25·649 - (0·1689A + 0·1073B)$ .  $x + 1·518y = A$ ;  $z = 6·117x$ , and  $z + 2·391w = B$ . On multiplying the quantity of cerotic acid by 6·117, we obtain the amount of myricin which when added to the former gives the percentage of wax. A mixture of 79·98 per cent. wax and 20·02 fat gave 11·30 per cent. cerotic acid, 69·12 myricin, 0·46 fatty acids, and 19·07 fat corresponding with 80·42 per cent. wax and 19·53 per cent. fat.

The sp. gr. of beeswax varies from 0·9625 to 0·9675. Paraffin and fat are lighter than beeswax, whilst the fatty acids and resin increase the sp. gr. of beeswax.

D. B.

## Technical Chemistry.

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**Consumption of Fuel for Heating Boilers.** By SCHEURER-KESTNER (*Dingl. polyt. J.*, **251**, 278—283).—A reply to Buute, who criticised the author's results on the heat of combustion of coal.

D. B.

**Analyses of Combustible Minerals.** By BOUSSINGAULT (*Ann. Chim. Phys.* [5], **29**, 363—392).—This paper contains an account of the examination of a variety of bitumens, lignites, &c.; the results of the analyses of which are contained in the following table:—

	C.	H.	O.	N.
Liquid bitumen of Bechelbronn .....	87·50	11·10	0·30	1·10
Bitumen of Bocanémé. ....	88·52	11·36	—	0·12
Bitumen of Schwabwiler. ....	85·38	12·33	2·17	0·12
Bitumen of Ambalema, Magdalena .....	88·31	9·64	1·68	0·37
Liquid bitumen, Hatten (Alsace) .....	87·40	12·60	—	—
Bitumen of Orinoco .....	77·93	7·94	13·87	0·26
Black naphtha of Balakhany .....	85·42	6·66	7·76	0·16
Bitumen of Bastennes. ....	85·74	9·58	2·88	1·80
Bitumen of Pont-du-Château .....	77·52	9·58	10·53	2·37
Bitumen of Abruzzi, Naples .....	81·83	8·28	8·83	1·06
Bitumen of Chinese fire-wells (filtered) .....	86·82	13·16	—	0·02
"      "      " (squeezed out) ....	82·86	13·09	4·06	—
Bitumen of Judæa .....	77·84	8·92	11·53	1·71
Asphalt of Coxitambo, Peru .....	87·75	9·68	2·58	—
Asphalt of Oran, Algeria .....	73·47	10·48	15·49	0·56
Asphalt of Egypt .....	85·29	8·24	6·22	0·25
Mineral wax of Baku, Russia .....	84·33	13·71	1·96	—
Fossil resin of Bucaramanga .....	82·70	10·80	6·50	—
Fossil resin of Santa-Rosa, Antioquia .....	77·80	9·60	12·57	0·03
Fossil resin of El Retiro, Antioquia .....	71·89	6·51	21·57	0·03
Copaline of Highgate .....	85·68	11·47	2·85	0·06
Copaline of India .....	85·73	11·50	2·77	—
Guayaquilite resin, Ecuador .....	77·66	8·20	14·80	—
Retinasphalt of Bovey-Tracy .....	74·12	8·18	17·51	0·19
Elaterite of Australia .....	72·15	10·30	16·84	0·71
Elaterite of Wallachia .....	69·70	10·19	19·40	0·71
Jonite of California .....	67·55	7·13	25·05	0·27
Torbanite of Scotland .....	82·30	10·50	5·00	2·20
Dysodil of Roth .....	69·01	10·04	19·25	1·70
Dysodil of Sicily .....	57·73	9·35	31·91	1·01
Lignite of Chile .....	79·24	5·50	13·69	1·57
Lignite of Antioquia .....	66·81	4·48	27·27	0·98
Bituminous lignite of Elboyen .....	77·04	7·81	12·65	1·86
Jet of Spain .....	81·98	5·81	11·53	0·68
Fibrous coal of Antioquia .....	87·05	5·00	6·56	1·39
Coal of Canoas, Bogota .....	80·96	5·13	12·50	1·41
Cannel coal of Montrambert .....	86·67	4·56	7·98	0·79
Fossil charcoal of Montrambert .....	86·67	4·56	7·98	0·79
Coal of Montrambert .....	82·33	3·52	12·52	1·65
Fossil charcoal of Blanzey .....	87·81	3·88	7·67	0·64
Anthracite of La Mure, Isère .....	95·26	2·51	1·56	0·67
Spheroidal anthracite .....	91·51	3·87	3·36	1·26
Anthracite of Borneo .....	93·66	2·94	2·88	0·52
Anthracite of Chile .....	92·25	2·27	4·94	0·56
Anthracite of Pembrokeshire .....	95·34	2·42	1·35	0·89
Anthracite of Muso .....	94·83	1·27	3·16	0·74
Adamantine anthracite .....	97·60	0·70	1·70	—
Graphite of Korschö. ....	97·87	0·37	1·70	0·06

P. P. B.

**Self-purification of Peaty Waters.** By W. N. HARTLEY (*Bied. Centr.*, 1883, 433—435).—Tidy refers the loss of organic matter which peaty water suffers to oxidation. The author quotes experiments made by himself which corroborate the statements of others, that the amount of organic matter which is oxidised is but small. With the



theory that the organic matter is carried down by suspended mineral matter, the author cannot fully concur, for although sandy clay and sand did not decolorise the water, yet magnesia and chalk had some action. Good results were obtained by the use of very hard spring-water, still better with aluminium sulphate, and the best by employing aluminic, ferric, and manganic hydroxides. E. W. P.

**Analysis of a Pit-water.** By O. ARCHE and C. HASSACK (*Dingl. polyt. J.*, 251, 132—135).—This water was drawn from the lignite mines at Wolleschnick in the domain of Frauenburg in Bohemia. The object of its examination was to ascertain whether it was serviceable as a feed-water for fish-ponds. The water had a dark-brown colour from the presence of much suspended matter. After filtration its colour was a pale yellow. 100,000 parts yielded 55·8 suspended matter composed of 24·4 inorganic and 31·4 organic matters. The former contained silicic acid, alumina, ferric oxide, lime, magnesia, sodium, and potassium silicates. The organic matter consisted mainly of coal.

100,000 parts of this water contained :—

Solid residue .....	20·51 parts
Residue after ignition .....	16·80 "
Total hardness .....	4·57°
Permanent hardness.....	1·78
Temporary hardness .....	2·79

From the results of the analysis given in the original paper, the authors are of opinion that the water is not suitable for the above purpose; a large proportion of organic matter is objectionable, since it would absorb the oxygen dissolved in the water and deprive the fish of this essential constituent. D. B.

**Preparation of an Antiseptic Compound.** By C. ASCHMANN (*Dingl. polyt. J.*, 251, 143).—For the preparation of this substance, called "antibacteride," the author heats 338 parts borax with 198 glucose, in the presence of a small amount of water. When the fusion is complete, he adds 124 parts boric acid, whilst constantly stirring, until it has been dissolved, and causes the liquor to evaporate at a gentle heat until a sample of it solidifies when run on a cold plate. The resulting mass is soft and translucent, forming an antiseptic suitable for the preservation of provisions. Its composition is represented by the formula  $C_6H_{12}O_6, Na_2B_4O_7, 3H_3BO_3$ . D. B.

**Use of Boric Acid for Preserving Food.** By J. FORSTER (*Dingl. polyt. J.*, 251, 170—172).—From a series of experiments made with a view to determine the action of boric acid on the animal system, the author draws the following conclusions: The admission of boric acid as addition to food, even in very small doses, is injurious to the digestive organs. This injurious action depends on the circumstance that boric acid acts so as to materially increase the proportion of solid matters and nitrogen in the fæces separated. It is also a remarkable coincidence that the action of boric acid on the intestinal

discharge is well marked, even by the exhibition of as little as 0.5 gram per diem. Moreover, this action is in direct relation to the quantity of acid taken, and is maintained for some time after the doses of acid have ceased. The action described is perceptible, not only with vegetable or animal foods, which contain a large proportion of indigestible ingredients, but also when highly digestible food, such as milk and eggs, is taken. Food to which boric acid has been added tends to cause an increase in the secretion of gall during assimilation. Its most important action, however, is the increase which it causes in the discharge of albuminous substances from the intestinal canal. From this it is evident that its use as a food preservative is not as beneficial as hitherto assumed. D. B.

**Process for Converting Liquid Mineral Acids into a Solid Form by the Addition of Kieselguhr.** (*Dingl. polyt. J.*, 251, 96.)

According to an invention patented by Vorster and Grüneberg, acids are mixed with kieselguhr or asbestos with a view to facilitate their transport. A mixture of 4 parts acid and 1 of kieselguhr forms a paste, which can be used for some operations without re-separation, e.g., sulphuric acid for the purification of paraffin and the preparation of carbonic anhydride for mineral water making. D. B.

**Utilisation of Phosphatic Slags.** By C. SCHEIBLER (*Dingl. polyt. J.*, 251, 191).—In order to oxidise the ferrous and manganous oxides in the slags from the basic process into ferric and ferrosiferrous, manganic and manganosomanganic oxides, and effect the decomposition of the sulphides, the author subjects the slag in pieces of fist-size to a careful roasting process in the presence of an abundant supply of air. The slag is then treated with water or steam, when, owing to the conversion of calcium oxide into calcium hydroxide, an extremely fine powder is obtained. By this treatment the slag is obtained in a more finely divided state than by mechanical means, i.e., pulverisation in disintegrators or other grinding machines. D. B.

**Process for Preparing Dichromates.** By T. ROEMER (*Dingl. polyt. J.*, 251, 192).—100 parts chrome ore are fused with 150 lime, 40 potash, and 30 soda. The melt is lixiviated with water, and the resulting liquor of potassium and sodium chromate treated with sulphuric or hydrochloric acid, the requisite amount of acid being calculated in accordance with the equation  $K_2Na_2Cr_2O_4 + H_2SO_4 = K_2Cr_2O_7 + Na_2SO_4 + H_2O$ . Potassium dichromate is formed, together with sodium sulphate, which is separated by evaporation. D. B.

**Utilisation of the Waste Waters from Wool Washing Works.** (*Dingl. polyt. J.*, 251, 230).—Referring to Fischer's process for lixiviating wool with water, and evaporating the resulting liquors for the recovery of potash, it is stated that 100 kilos. of wool produce 80 liters of liquor of 10° B. 100 liters of this liquor give 6.5 kilos. residue by evaporation containing about 70 per cent. potash.

Delattre evaporates the liquors to a density of from 10 to 12° B., and fuses the residue. The resulting crude potash contains

$K_2CO_3$ .	$K_2SO_4$ .	KCl.	$Na_2CO_3$ .	Insoluble.	Loss.
80	6	4	3	5	2

After the extraction of the suint the wool is washed, the resulting soap waters being treated with hydrochloric acid and ferric chloride for the recovery of the fatty acids.

According to Braun, the separation and purification of suint is effected by treating the sweat of wool with water. Thus a compound called "lanoline" is obtained, which when heated splits up into suint and water. Suint is suspended in the wool washings in the form of lanoline, and is separated by passing the wash waters through hydro-extractors. The mass is purified by washing it with water, heating and decanting the fat; by rinsing the latter with water, white lanoline is obtained. With water, commercial suint forms sodium carbonate or hydroxide, soap, and a milky substance from which lanoline is obtained when the mixture is subjected to the above treatment.

Lortzing precipitates the suint from wool wash-waters with lime and ferrous sulphate, and utilises the resulting sludge for the preparation of bituminous cement. The pressed sludge is dried, ground, mixed with 15 per cent. suint, and heated to  $200^\circ$ , after which it is treated with an equal weight of calcium carbonate. D. B.

**Influence of Titanic Acid on the Fusibility of Refractory Earths.** By H. SEGER (*Dingl. polyt. J.*, 251, 94).—100 parts of Zettlitz kaolin of 98.5 per cent. purity were mixed with from 5 to 10 per cent. of silicic acid on the one hand, and an equivalent amount of titanic acid on the other hand. The mixture was formed into small cones and exposed in Deville's blast furnace to a temperature between those at which wrought iron and platinum melt. Treated in this manner, the kaolin gave a white hard mass of well-defined form, translucent at the edges, and with a dull surface. 100 parts kaolin mixed with 5 parts silicic acid gave a well-defined form, snow-white in colour, somewhat porous, translucent at the edges, dull surface, and giving on fracture a porcelain-like appearance. A mixture of 100 parts kaolin with 10 parts silicic acid gave a similar result, but a more porous product on fracture resembling porcelain still more closely. The cone composed of a mixture of 100 parts kaolin with 6.65 titanic acid had a bluish-grey glazed surface, and proved on fracture to have thoroughly sintered together. 100 parts kaolin, mixed with 13.3 titanic acid, fused completely to a dark bluish-grey bead of enamel.

Hence the presence of titanic acid has an influence on the fusibility of refractory clays which is exactly the reverse of that which silicic acid exerts, the conditions of temperature being the same. It is therefore important to take into consideration the amount of titanic acid present in earths to be employed as refractory materials. It is not improbable that the bluish-grey colour which some clays develop when heated very strongly is due to the presence of titanic acid. D. B.

**Process for Preparing Ochre Colours.** By S. H. COHN (*Dingl. polyt. J.*, 251, 240).—The author obtains ochre pigments by treating

a mixture of lead oxide and chloride with nitric acid, aluminium sulphate, and potassium dichromate. He then adds water, and introduces sulphuretted hydrogen into the mixture until the desired tint is obtained. D. B.

**Application of Electricity in Chemical Industry.** By F. FISCHER (*Dingl. polyt. J.*, **251**, 28—32).—The practical difficulty of utilising electricity for metallurgical purposes has been its cost of production, although since the introduction of dynamo-machines the application of electricity in metallurgy has made more progress.

According to Kohlrausch, a current of 1 weber deposits 6.779 mgrms. of silver per minute, whilst 1 ampère (= 10 webers) corresponds to 3.96 grams silver per hour in a cell. For practical purposes it may be assumed that a current of 100 ampères deposits 1 mgrm.-equivalent of the various substances per second. Thermochemical researches have, however, given different values to the various compounds, *e.g.* :—

Reaction.	Heat of formation of the compound.	Heat of solution of the compound.	Heat of formation in aqueous solution.
Zn.Cl <sub>2</sub> .....	97,210	+ 15,630	112,840
Cd.Cl <sub>2</sub> .....	93,240	+ 3,010	96,250
Cu <sub>2</sub> .Cl <sub>2</sub> .....	65,760	—	—
Cu.Cl <sub>2</sub> .....	51,630	+ 11,080	67,710
Hg.Cl <sub>2</sub> .....	63,160	— 3,300	59,860
Au.Cl <sub>3</sub> .....	22,810	+ 4,450	27,260
Sn.Cl <sub>2</sub> .....	80,790	+ 350	81,140
Sn.Cl <sub>4</sub> .....	127,240	+ 29,920	157,160
Zn.O.SO <sub>3</sub> .Aq ..	—	—	106,090
Cu.O.SO <sub>3</sub> .Aq ..	—	—	55,960
Ag <sub>2</sub> .O.N <sub>2</sub> O <sub>5</sub> .Aq..	—	—	16,780

Kiliani is of opinion that the electromotive force of a Daniell's element is equivalent to the difference of the thermal values corresponding with the chemical processes involved therein, *i.e.*, 106,090 — 55,960 = 50,130 cal. Assuming that the E.M.F. of a Daniell's element is equal to 1.12 volts, 1 volt would be equal to 44,760 cal., and it would therefore be possible to calculate the E.M.F. from the thermal units, *e.g.* :—

Compound.	Calorific value.	E.M.F. calculated therefrom.
Ag <sub>2</sub> .O.N <sub>2</sub> O <sub>5</sub> .Aq .....	16,780	0.37 volt.
Ag <sub>2</sub> .O.SO <sub>3</sub> .Aq .....	20,390	0.46 „
Cu.O.N <sub>2</sub> O <sub>5</sub> .Aq .....	52,410	1.17 „
Cu.O.SO <sub>3</sub> .Aq .....	55,960	1.25 „

The deposition of pure silver from a mixed solution of the sulphates or nitrates of silver and copper would be effected by the use of an E.M.F. of 1.17 and 1.25 volts respectively. Braun has, however, shown that a part only of the heat of combination is transformed into current energy; whilst Jahn found that in spite of the different amounts of chemical work which must be supplied by the current for

the decomposition of, *e.g.*, zinc and copper sulphates, the entire loss of energy in the circuit is the same in both cases, for in the deposition of 1 kilo. copper and 1 kilo. zinc, 1807 and 977 cal. are developed, corresponding with—

	Free heat.	Chemical work.	
ZnSO <sub>4</sub> ....	63,216 cal.	+ 106,090 cal.	= 169,306 cal.
CuSO <sub>4</sub> ....	114,744 „	+ 55,960 „	= 170,704 „

The total amount of electricity abstracted from the battery during the decomposition was equal to 170,000 cal. (approximately). When no chemical work is done, that is, when the platinum electrodes are replaced by zinc and copper electrodes, the amount of heat liberated in the decomposition of CuSO<sub>4</sub> is equal to 78,994 cal., and in the case of ZnSO<sub>4</sub> to 79,916 cal.

According to Kiliani, the following ores are good conductors of electricity:—Tin ore, silver glance, red silver, galena, copper glance, purple copper, copper pyrites, sulphuretted ores of nickel and cobalt, and iron pyrites. The following are bad or non-conductors:—Grey antimony ore, tin pyrites, white lead ore, red copper ore, malachite, lasurite, grey copper ore, blende, and calamine. D. B.

**Investigations on the Welding of Iron.** By E. P. BOEHME (*Dingl. polyt. J.*, 251, 71—77).—In 1880 the German Society for Promoting Technical Industry appointed a commission to inquire into the capacity of different kinds of iron for welding. The author now gives an account of the experiments which were made, and of the results which were obtained. The samples of iron experimented with were prepared from the same material (ingot iron from the Gutehoffnungs Hütte), and consisted of a series of unwelded and welded round bars. Experiments were made also with bars from ordinary Silesian iron.

The subjoined table (p. 787) gives the results of the investigation.

In comparing these results with the chemical constitution, the following conclusions are arrived at:—The molecular adjustment of iron has a much greater influence on its capability of being welded than the amount of carbon present. This property of iron increases with the amount of silicon, and decreases with that of the manganese present. This is due to the fact that during the oxidation in the welding operation the silicon produces a slag which dissolves the resulting ferrosferic oxide. In the case of ingot iron, it was found that the amount of silicon was the same before and after welding, and it is not improbable that the modified condition in which this element is present in ingot iron explains this want of influence on the welding property. Whilst Ledebur supposes that the total amount of foreign constituents in unwelded iron is about 70 per cent. greater than in welded iron, the results of the present investigation show that the percentage of silicon, phosphorus, carbon, and manganese in the harder kinds of ingot is 0.717, in the softer kinds 0.423, and in weld iron 0.520. According to Reiser the welding of iron is influenced by the chemical constitution, inasmuch as its molecular condition, that is, the property of crystallising, depends thereon.

Properties.	Hard ingot iron.		Soft ingot iron.		Silesian weld iron.	
	Not welded.	Welded.	Not welded.	Welded.	Not welded.	Welded.
Tensile strength (kilos. per sq. mm.) . . . . .	50·7	29·4	45·4	32·2	40·7	33·1
Expansion in per cent., calculated—						
1. On 100 mm., i.e., 50 mm. on each side of the fractured place . . . . .	24·6	3·7	29·9	5·8	26·1	8·1
2. On 200 mm., i.e., 100 mm. on each side of the fractured place . . . . .	20·8	3·2	25·1	5·1	22·2	7·7
Transverse contraction in per cent. of the original diameter . . . . .	34·9	4·5	44·7	10·5	39·5	14·0

In conclusion, it is recommended to abstain from welding ingot iron, as it can be cast with ease into any form or size. D. B.

**Evolution of Gas from Steel Castings.** By F. MÜLLER (*Dingl. polyt. J.*, 251, 83—91).—Contrary to Pourcel's assumption that the gas evolved from steel castings consists of carbonic oxide, the author found only hydrogen and nitrogen in the occluded gases given off from steel ingots. Pourcel has, however, recently shown that the gas evolved during the solidification of steel contains the more hydrogen the richer the metal is in manganese. The author is of opinion that the rising of steel in the mould is due to the presence of hydrogen, whilst the frothing and crackling is attributed to the absorption of carbonic oxide, which escapes in the form of bubbles of gas when the fluid metal has been reduced to the solidifying temperature. The basic metal, without any addition, contains mainly hydrogen and nitrogen, and small quantities of absorbed carbonic oxide, hence it is more quiescent in the mould, although it shows a great tendency to rise. Carbonic oxide is formed on adding spiegeleisen or ferromanganese, and the steel being saturated with the gas, then froths up, and emits gas bubbles until it begins to solidify, when hydrogen is again evolved. When silicide is added steel may be formed without the evolution of carbonic oxide. Whilst the author assumes that silicon augments the solubility of the gases in steel, and Pourcel supposes that it diminishes or annuls it, Brustlein is of opinion that silicon and manganese render the steel more porous, so that the gases are better able to pass through the mass of cast metal.

In conclusion, it is stated that if the formation of bubbles is attributed to the presence of hydrogen, it is essential to conduct the final operation in connection with the casting of steel in dry air; on the

other hand, if carbonic oxide is the gas evolved, the decomposition should be effected by silicon, which will destroy the bubbles.

D. B.

**Zinc from Pyrites Residues.** By M. J. CREUTZ (*Chem. News*, 49, 62—63).—In one process for recovering the zinc from pyrites residues, the burnt ore is lixiviated, the lixivium concentrated to crystallising point, mixed with sodium chloride in quantity equal to the zinc sulphate dissolved, whereupon sodium sulphate is deposited. When the concentration reaches 50° B., various ferrous and sodium sulphates separate out, and zinc chloride remains in solution. None of these separations are sharply indicated, nor are the reactions as simple as they appear, and therefore the dry residue from the last solution contains about 85 per cent. zinc chloride and 15 per cent. sodium salts. It is for this reason unsuitable for the preservation of wood; it can, however, be used with advantage for the preparation of zinc hydroxide to be used in desulphuring alkaline lyes; for this purpose it is simply necessary to treat with milk of lime, and separate and wash the precipitated zinc oxide.

In another process, the burnt ores are exposed to the air in order to further oxidise the iron, manganese, and sulphurous acid; they are then systematically extracted in a series of tanks, so that the final solution is of 20° B., contains scarcely any iron and only traces of manganese and cobalt. This is mixed with calcium chloride solution 15° B., and the calcium sulphate separated; the filtrate (10° B.) is evaporated, chloride of lime added to precipitate the manganese and cobalt, and at 48° B. the whole of the calcium sulphate separates and the solution contains zinc chloride mixed with a small quantity of sulphate. This process yields a zinc chloride applicable to all purposes; but it has the drawback of being very dilute, and does not produce any saleable by-product like the sodium sulphate in the above process. The removal of zinc and sulphur from the burnt ore increases its value for subsequent metallurgical treatment.

D. A. L.

**Process for Preparing Hydrocarbons.** By E. HEUSSER (*Dingl. polyt. J.*, 251, 192).—For the preparation of low-boiling hydrocarbons, the author subjects coal to destructive distillation and the simultaneous action of gaseous chlorine and hydrochloric acid gas. High-boiling hydrocarbons are obtained by subjecting a mixture of coal and zinc chloride, or coal, coal-tar, and zinc chloride, or coal, coal-tar oil, and zinc chloride, to destructive distillation in a current of hydrochloric acid gas.

D. B.

**Products of the Dry Distillation of Wood at Low Temperatures.** By C. F. MABERY (*Amer. Chem. J.*, 5, 256—263).—Three samples of crude methyl alcohol, prepared in the manufacture of acetic acid by the dry distillation of wood at low temperatures, were examined; they were collected (a) at the beginning of the distillation, (b) after several hundred gallons had distilled, and (c) when the distillation of methyl alcohol was well advanced. These samples were subjected to fractional distillation. The most volatile portion in each

case was proved to be acetaldehyde. The fraction boiling at 25—40° from (a) was shown to contain methyl formate, which has not hitherto been recognised as a constituent of wood-spirit; the presence of methylal could not be determined. The fraction 50—54° from (a) gave reactions for aldehyde and acetone, and fractions 54—56° from (a) and from (b) were nearly pure methyl acetate. The bulk of the methyl alcohol was found in fraction 65—68° from (c). Dimethyl-acetal could not be detected. The amount of acetone—which affects the value of wood-spirit for preparing dimethylaniline—was determined in several portions by Kramer's method; the amount found varying from 1·04 to 3·41 per cent., is smaller than is usual in wood-spirit. Allyl alcohol could not be detected. For want of material, the high boiling oils were not completely examined; they contain furfuraldehyde, pyroxanthine in small quantity, as also methyl ethyl ketone and allyl acetate.

H. B.

**Pasteurising Barrelled Beer.** By G. BEHREND (*Bied. Centr.*, 1883, 502).—The principal points to be observed are the following:—Filter off the albuminous matter, which separates while the beer is heating, and run the hot beer under pressure direct into the storage vessel, avoiding contact with the air, in order to prevent the introduction of deleterious germs. The author prefers to employ barrel-shaped glass carboys. The filling under pressure is an important factor, as the pressure subsequently increases in the closed vessel, and helps to preserve the beer.

D. A. L.

**Fermentation Experiments with Gluten instead of Diastase in the Mash.** By G. HEINZELMANN (*Bied. Centr.*, 1883, 503).—150 grams of rye-groats were made up to 1 litre with water warmed at 60° C. for one hour, then cooled to 30°, and mixed with 20 grams compressed yeast containing starch, for fermentation. In almost all experiments, a large amount of acid was formed. In two cases, when sulphuric acid had been added, the quantity of acid produced was very small; the fermentation, however, was very weak. In fact, the action of gluten on starch was almost completely destroyed.

D. A. L.

**Mashing Temperature and the Favourable Temperature for Yeast Sowing.** By STENGLEIN (*Bied. Centr.*, 1883, 503).—The practical results of the author's experiments are in brief:—For mashing good malt, 61·25° is recommended, and for bad and injured malt 61·25—65°; the temperature should not systematically increase either during mashing or fermenting. A temperature of 61·25° kills globular bacteria, and consequently prevents formation of liquid acids. The most favourable temperature for the production of lactic acid is 45—61·25°, and the presence of a sufficient quantity of this acid in the yeast stops the development of butyric acid. The favourable temperature for sowing yeast is 50°.

D. A. L.

**Strong Yeast.** By G. HEINZELMANN (*Bied. Centr.*, 1883, 502—503).—In this note, the following scheme is described for the preparation of a very active and durable yeast. For this purpose a large vat



(2900 litres capacity), 2 barrels (154 litres capacity), and a cask (34 litres capacity) of yeast are required. In the afternoon, a mash is prepared in one of the barrels from 25 kilos. of green malt and hot water: the following morning another mashing is made in the second barrel with 12.5 kilos. green malt, 2 buckets of the preceding mash, and hot water. The first mashing is continued until the following morning, when it is somewhat sour, the second until 1 o'clock (night). The former is thoroughly well mixed at 8 P.M. with the yeast, and the yeast-cask is refilled with the mixture, which in its turn is added to the contents of the second barrel at 4 A.M. The yeast is removed at 7 A.M. from the first barrel, the contents of both barrels are then mixed together, and distributed equally over it. The yeast then remains until the fresh mash is cooled for mixing.

D. A. L.

**Utilisation of Malt Combing in the Manufacture of Pressed Yeast.** By L. HAYDUCK (*Dingl. polyt. J.*, **251**, 287).—100 grams malt combings are boiled in water for half an hour, and filtered. The filtrate is treated with 100 grams sugar, and diluted to 1 litre. 10 grams pressed yeast (containing 78.35 per cent. moisture) are then added. The mixture is allowed to ferment at 17.5°. The nitrogen before fermentation was equal to 0.0947 per cent., whilst after fermentation it amounted to 0.0474 per cent., so that 50 per cent. had been assimilated by the yeast. The weight of yeast after fermentation was 39.7 grams, hence 29.7 grams had been newly formed.

D. B.

**Nitrogenous Constituents of Barley and Malt.** By C. LINTNER (*Dingl. polyt. J.*, **251**, 225—228).—The author is of opinion that the total amount of nitrogen in barley or malt bears no relation to the diastatic action. The quantity of soluble albumin, however, is of some value in determining this point. By assuming that the soluble albuminous nitrogen belongs to the diastase—an hypothesis which is quite justifiable—and that the diastase is closely related to the albuminoids (so that on multiplying by 6.25 we obtain nitrogen corresponding to diastase), the quantity of diastase in malt amounts to about 2 per cent. on the dry substance. 1 part of diastase is capable of converting 400 parts of starch into sugar in 20 minutes. In practice the following proportions hold good:—100 parts dry malt substance corresponding to 166 green malt containing 40 per cent. moisture contain 2 parts diastase capable of saccharifying 800 parts starch in 20 minutes. 166 parts green malt convert 800 parts starch into sugar, or 0.2075 converts 1 of starch. When potatoes containing 18 per cent. starch are used, the saccharification of 18 kilos. starch from 100 kilos. potatoes would require the addition of  $(18 \times 0.2075) = 3.735$  kilos. malt exclusive of the quantity necessary for the preparation of yeast.

D. B.

**Refining of Sugar and Molasses by Means of Concentrated Acetic Acid.** By A. WERNICKE (*Bied. Centr.*, 1883, 502).—Pure sugar scarcely dissolves in concentrated acetic acid, whilst all the impurities of cane-sugar are readily soluble in it. In the present process, dry cane-sugar is heated at about 70° in closed vessels with

50—70 per cent. of its weight of concentrated acetic acid or molasses concentrated to 45—50° B. with 75 to 90 per cent. When cool the acetic acid is poured off, and the sugar machined and dried, when it is ready for the market. The acetic acid is recovered by distillation.

D. A. L.

**Loss in the Beet-sugar Manufacture.** (*Bied. Centr.*, 1883, 491—492.)—In grating the beets previous to pressing, lumps and clots form, which are not sufficiently pressed in the subsequent operation. This occasions a loss of sugar of considerable monetary value. It is therefore advisable to rub the material from the press through a sieve, sprinkling water over it, repressing the portions which run through, and also to break up the lumps and repress them when disintegrated.

D. A. L.

**Purification of Saccharine Juices.** (*Dingl. polyt. J.*, 251, 191.) Schott treats beet-juice with a solution of potash-water glass, and heats the mixture. He then adds sulphurous acid, and completes the neutralisation with dilute sulphuric acid. The filtrate is treated with 1·82 parts of gypsum to 1 part of potassium hydroxide contained therein; it is then evaporated to a syrupy consistence and filtered. After standing for some time, the sugar crystallises out completely from the solution.

Eachrau recommends the treatment of saccharine juices with from 0·5—6 per cent. manganous oxide, manganic dioxide, manganese sulphate, &c. Allow to settle, filter, add about 5 per cent. lime, remove the excess with carbonic anhydride or sulphurous acid, filter through animal charcoal, and evaporate.

D. B.

**The Working of a Sugar Refinery.** By G. STADE (*Dingl. polyt. J.*, 251, 127—132).—The author gives a detailed account of a year's working of a sugar refinery, which dealt with raw sugar from the district of Magdeburg and Brunswick. The total quantity of crude sugar which was worked up during that period amounted to 5777·3 tons, the average composition being:—

		In 100 parts of dry substance.	To 100 parts sugar.
Sugar .....	96·39	97·96	—
Water .....	1·60	—	—
Non-saccharine matter..	2·01	2·04	2·09
Ash contained therein ..	0·99	1·01	1·03

Of this quantity 1878·9 tons were worked up in the crude form, whilst 3898·4 tons were machined. The first and second products of the refinery were filtered through 10,583 tons of animal charcoal, 18·32 tons being used for 10 tons of crude sugar. The charcoal had the following composition:—

H <sub>2</sub> O.	C.	Insoluble in HCl.	CaCO <sub>3</sub> .	CaSO <sub>4</sub> .	CaS.	Undeter- mined.
1·93	6·23	0·72	8·16	0·45	0·03	82·48

When heated with potash it yielded a solution having a pale yellow

colour. After use it was boiled out on the filters with soda-ley, or a mixture of soda and ammonia. The boilers were worked with West-phalian coal, containing 1·9 per cent. of water and 10·8 per cent. ash. The consumption of fuel was 144·7 parts for every 100 parts of crude sugar passed through the works. This large amount is due to inferiority of the coal and defects in the plant and machinery.

The following statistics are given as to the actual working of the refinery:—

Candy, white and half white.....	975·579 tons or 16·98 p.c. on the raw sugar.			
Candy, yellow and dark yellow .....	87·981	„	1·52	„ „
Lump sugar, in loaves of 12·5 k. ....	1424·615	„	24·66	„ „
Lump sugar, crushed	1591·965	„	27·55	„ „
Lump sugar, in cubes	1021·250	„	17·68	„ „
Brown sugar .....	118·667	„	2·06	„ „
Osmose water, concentrated .....	81·000	„	1·40	„ „
Syrup .....	316·250	„	5·47	„ „
Total mass ....	5617·307	„	97·23	„ „

By deducting this sum from the total amount of raw sugar passed into the works, *i.e.*, 5777·3 tons, a loss of 159·993 tons, or 2·77 per cent., is obtained. In order to determine the loss of sugar and non-sugar, the following figures are given:—

	Sugar.	Ash.	Non-sugar.
Candy .....	1063·560 tons	—	—
Lump sugar.....	4037·830 „	—	—
Brown sugar ....	109·767 „	2·136 tons	3·560 tons
Osmose water ....	34·115 „	15·236 „	18·290 „
Syrup .....	179·029 „	30·961 „	53·320 „
Passed out of refinery.....	5424·300 „	48·333 „	75·170 „
Passed through works .....	5568·700 „	57·195 „	58·929 „
Difference.....	—144·400 „	—8·862 „	+16·241 „

The loss of pure sugar was—

In the charcoal .....	28·786 tons
In the sweet waste water .....	37·430 „
In other operations.....	78·222 „

Total loss..... 144·438 „

For every 100 parts of loss—

19·33 took place in the animal charcoal,  
25·92 in the sweet waste water, and  
54·15 in other stages of the process.

The loss in 100 parts of pure sugar was 2·59 or 2·50 in 100 parts of raw sugar. Of the mineral constituents, a loss of 8·862 tons took place, which amount passed out of the refinery in the processes of filtration.

The following numbers will give a clear idea of the actual yields obtained:—

*Produced.*

5101·390 tons refined sugar	+	97·900 tons from brown sugar.
81·000 „ osmose water	+	3·314 „ „
316·250 „ syrup	+	13·299 „ „
159·993 „ loss	+	4·154 „ „

*Yield.*

Refined sugar .....	5199·290 tons, or 90·00 per cent.
Osmose water .....	84·314 „ 1·46 „
Syrup.....	329·549 „ 5·70 „
Loss .....	164·147 „ 2·80 „

Total weight of raw sugar converted }	5777·300 tons.
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If the syrup and osmose water be brought under the one heading of syrup, we obtain 90·00 per cent. refined sugar, 7·16 per cent. syrup, and 2·84 per cent. loss.

Yield obtained from the pure sugar contained in the raw sugar passed into the works:—

5199·290 tons refined sugar at 100 per cent. pure sugar .....	5199·290 tons.
84·314 tons osmose water at 42·13 per cent. pure sugar .....	35·522 „
329·549 tons syrup at 56·61 per cent. pure sugar .....	186·558 „
Total obtained .....	5421·370 „
Pure sugar contained in raw sugar	5568·739 „
Loss of polarising substance.....	147·369 „

Hence the yield for 100 parts of pure sugar was 93·366 refined sugar, 0·638 osmose water, 3·346 syrup, and 2·650 loss, or by calculating osmose water and syrup as syrup, 93·366 refined sugar, 3·984 syrup, and 2·650 loss, or by regarding the osmose water as loss, 93·366 refined sugar, 3·346 syrup, and 3·288 loss. D. B.

**Bleaching Flax and Hemp Tissues.** (*Dingl. polyt. J.*, 251, 228.)—According to Delaboue, the threads or tissues are subjected to

successive boilings in alkaline liquors to remove pectinic substances from the cellulose. They are then passed through a solution of chloride of lime and a solution of aluminium sulphate, saturated with aluminium hydroxide. If required perfectly white, they are boiled in soap solution and ammonia, and subjected to a second treatment.

D. B.

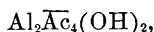
**Contributions to the Chemistry of Mordants.** By L. LIECHTI and W. SUIDA (*Dingl. polyt. J.*, **251**, 177—185).—The authors have investigated the dissociation ratios of the most important salts of alumina and ferric oxide used as mordants. The normal and basic sesquioxide salts of one and the same acid, as well as various acids (*e.g.*, thioacetates), were experimented with, and in speaking of dissociation, the authors mean decomposition which is observed externally, and characterised by the separation of an *insoluble* compound. Two expedients were adopted to produce this result: Dilution with water, and heating the respective aqueous saline solutions. It is thought that the following data will be of great service to the dyeing and printing industry.

To study the behaviour of aluminium sulphates, the compounds  $\text{Al}_2(\text{SO}_4)_2(\text{OH})_2$  and  $\text{Al}_4(\text{SO}_4)_3(\text{OH})_6$  were examined, in addition to the normal sulphate. They were obtained by deoxidising the normal salt with  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$ , so that sodium sulphate was simultaneously present in the solutions. Concentrated solutions were composed of 200 grams  $\text{Al}_4(\text{SO}_4)_3$ , whilst dilute solutions contained 150 grams of the normal salt.  $\text{Al}_2(\text{SO}_4)_3$  is not altered by dilution with water or when heated.  $\text{Al}_2(\text{SO}_4)_2(\text{OH})_2$  in concentrated solutions remains unaltered when heated, whilst in dilute solutions it splits up after being boiled for half an hour, a permanent precipitate being formed.  $\text{Al}_4(\text{SO}_4)_3(\text{OH})_6$  is decomposed in concentrated solutions at  $65^\circ$ , and in dilute solutions at  $55^\circ$ , with the formation of permanent precipitates. At  $100^\circ$  both solutions are gelatinised. In mordanting, drying, and ageing the following quantities of alumina are retained in an insoluble form by the fibre:  $\text{Al}_2(\text{SO}_4)_3$  13 per cent.,  $\text{Al}_2(\text{SO}_4)_2(\text{OH})_2$  51 per cent., and  $\text{Al}_4(\text{SO}_4)_3(\text{OH})_6$  58 per cent.

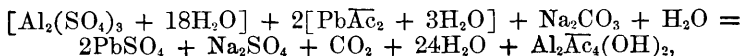
To investigate the behaviour of aluminium sulphacetates, the following salts were prepared from the normal sulphate:— $\text{Al}_2\text{SO}_4\text{Ac}_4$  by means of lead acetate,  $\text{Al}_2\text{SO}_4\text{Ac}_3(\text{OH})$  by means of lead acetate and sodium carbonate,  $\text{Al}_2\text{SO}_4\text{Ac}_2(\text{OH})_2$  by means of lead acetate and sodium bicarbonate, and  $\text{Al}_2\text{SO}_4\text{Ac}(\text{OH})_3$  by means of lead acetate and acetic acid. The salts are gelatinised at  $100^\circ$ . The first is decomposed at  $89^\circ$  in concentrated solutions, whilst the dissociation of the other salts depends on the extent of their basicity, the last salt decomposing at  $48^\circ$  in concentrated solutions, and at  $40^\circ$  in dilute solutions. In mordanting, drying, and ageing nearly the whole of the alumina contained in these salts is retained by the fibre in an insoluble form.

In the next place, the authors studied the action of aluminium acetates, the normal salts being prepared from aluminium sulphate and lead acetate. The basic salts were obtained by the addition of sodium bicarbonate to the normal acetate. The solutions contained 200 grams  $\text{Al}_2(\text{SO}_4)_3 + 18\text{H}_2\text{O}$  in 1 liter.  $\text{Al}_2\text{Ac}_6$  is not decomposed

when heated.  $\text{Al}_2\overline{\text{Ac}}_3\text{OH}$  is split up when boiled for a short time, and at  $100^\circ$  yields a permanent precipitate.  $\text{Al}_2\overline{\text{Ac}}_4(\text{OH})_2$  is decomposed at  $74^\circ$ ,  $\text{Al}_2\overline{\text{Ac}}(\text{OH})_3$  at  $56^\circ$ , and  $\text{Al}_2\overline{\text{Ac}}_2(\text{OH})_4$  at  $44^\circ$ . The salts are not altered when diluted with water. The compound,



when prepared from the normal sulphate by the addition of lead acetate and sodium carbonate, according to the equation—



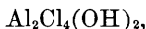
begins to decompose at  $65^\circ$ , and differs from the acetates described in the above by being split up when diluted with water. Dilution in the case of the other acetates raises the dissociation ratio. In mordanting, drying, and ageing, the normal acetate gives up half its alumina to the fibre; whilst the alumina of the salt,  $\text{Al}_2\overline{\text{Ac}}_4(\text{OH})_2$ , obtained from aluminium sulphate by means of lead acetate and sodium carbonate, is completely deposited in the fibre.

In regard to the behaviour of aluminium thiocyanates, the following observations were made: The normal thiocyanate was prepared by double decomposition of  $\text{Al}_2(\text{SO}_4)_3 + 18\text{H}_2\text{O}$  and  $\text{Ba}(\text{CNS})_2 + 2\text{H}_2\text{O}$ , and from it the basic salts were obtained by deoxidation with sodium bicarbonate. The solutions of the normal salt corresponding with 200 grams aluminium sulphate per liter remained clear at all temperatures. The following salts were prepared:—



The compound,  $\text{Al}_2(\text{CNS})_5\text{OH}$ , is not altered when heated; whilst the more basic compounds are decomposed on boiling. Dilution with water does not affect any of the thiocyanates. Only 33 per cent. of  $\text{Al}_2(\text{CNS})_6$  is fixed on the fibre.

The behaviour of aluminium chloride was then investigated. The normal salt was prepared by dissolving aluminium hydroxide in the theoretical quantity of hydrochloric acid. The basic compound,



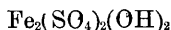
was obtained by heating  $\text{Al}_2\text{Cl}_6$  with aluminium hydroxide, thus:— $2\text{Al}_2\text{Cl}_6 + \text{Al}_2(\text{OH})_6 = 3\text{Al}_2\text{Cl}_4(\text{OH})_2$ . By carrying the deoxidation still further, i.e., introducing more  $\text{Al}_2(\text{OH})_6$  than the quantity represented by the above equation, decomposition takes place, a solution being formed which contains free hydrochloric acid in addition to  $\text{Al}_2\text{Cl}_6$ , whilst alumina is deposited. When a solution of aluminium chloride, corresponding with 200 grams  $\text{Al}_2(\text{SO}_4)_3 + 18\text{H}_2\text{O}$  in 1 liter, is treated with sodium carbonate, the deoxidation may be carried gradually from  $\text{Al}_2\text{Cl}_6\text{OH}$ ,  $\text{Al}_2\text{Cl}_4(\text{OH})_2$  and  $\text{Al}_2\text{Cl}_3(\text{OH})_3$  to  $\text{Al}_2\text{Cl}_2(\text{OH})_4$ . On heating it is possible to obtain even the compound  $\text{Al}_2\text{Cl}_3(\text{OH})_3$ . The soluble aluminium chlorides are not altered when heated or diluted. The compound,  $\text{Al}_2\text{Cl}_2\overline{\text{Ac}}_4$ , is recommended by the authors as a mordant in printing with alizarin. It is prepared in accordance

with the equation  $\text{Al}_2(\text{SO}_4)_3 + 18\text{H}_2\text{O} + 2\text{Pb}\overline{\text{Ac}}_2\cdot 3\text{H}_2\text{O} + \text{BaCl}_2\cdot 2\text{H}_2\text{O} = \text{BaSO}_4 + 2\text{PbSO}_4 + 26\text{H}_2\text{O} + \text{Al}_2\text{Cl}_2\overline{\text{Ac}}_4$ , corresponding with 200 grams of aluminium sulphate, 227.6 lead acetate, and 73.3 barium chloride for 1 liter of mordant of  $7.8^\circ \text{B}$ ; the product can be heated or diluted without decomposition. In mordanting, drying, and ageing, only 3.26 per cent. of the alumina contained in this mordant is given up to the fibre in an insoluble form.

Aluminium nitrate,  $\text{Al}_2(\text{NO}_3)_6$ , is obtained from the normal aluminium sulphate and lead nitrate, and gives the following compounds when treated with sodium bicarbonate:— $\text{Al}_2(\text{NO}_3)_5\text{OH}$ ,  $\text{Al}_2(\text{NO}_3)_4(\text{OH})_2$ ,  $\text{Al}_2(\text{NO}_3)_3(\text{OH})_3$ , and  $\text{Al}_2(\text{NO}_3)_2(\text{OH})_4$ . By continuing the addition of alkali, a gelatinous precipitate was obtained. The behaviour of these mordants is analogous to that of the corresponding chlorides.

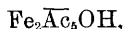
Referring to aluminium phosphate, the authors mention that sodium phosphate,  $\text{Na}_2\text{HPO}_4$ , does not produce a precipitate when treated with an excess of aluminium sulphate. They found that it requires 2 mols. of aluminium sulphate to keep 1 mol. of aluminium phosphate in solution.

*Behaviour of Ferric Oxide Salts.*—Normal ferric sulphate,  $\text{Fe}_2(\text{SO}_4)_3$ , can be deoxidised with sodium bicarbonate until the compound



is formed; the latter, however, decomposes in a few hours. The same applies to a solution of ferric sulphate corresponding with 200 grams aluminium sulphate per liter. By doubling the strength of the solution, the addition of alkali can be carried on to form the compound  $\text{Fe}_4(\text{SO}_4)_4(\text{OH})_6$ , which is a very unstable salt.  $\text{Fe}_2\text{Cl}_6$  can be deoxidised to  $\text{Fe}_2\text{Cl}(\text{OH})_5$ .

Normal ferric acetate was prepared from  $\text{Fe}_2(\text{SO}_4)_3$  and lead acetate. By the removal of acid by means of sodium carbonate, the solutions of the following compounds can be obtained:— $\text{Fe}_2\overline{\text{Ac}}_5\text{OH}$ ,  $\text{Fe}_2\overline{\text{Ac}}_4(\text{OH})_2$ ,  $\text{Fe}_2\overline{\text{Ac}}_3(\text{OH})_3$ , and  $\text{Fe}_2\overline{\text{Ac}}_2(\text{OH})_4$ . The normal ferric acetate can be heated or diluted without change. The solutions of the basic salts correspond with 100 grams  $\text{Al}_2(\text{SO}_4)_3$  in 1 liter. The first salt,



is decomposed at  $86^\circ$ , and the last,  $\text{Fe}_2\overline{\text{Ac}}_2(\text{OH})_4$ , at  $70^\circ$ . D. B.

**Substitute for Tartar Emetic in Dyeing.** (*Dingl. polyt. J.*, **251**, 48.)—Tartar emetic is being gradually replaced in dyeing and printing by a new antimony preparation consisting of potassio-antimonic oxalate,  $\text{C}_6\text{O}_{12}\text{SbK}_3 + 6\text{H}_2\text{O}$ . It is obtained by saturating a boiling solution of hydrogen potassium oxalate (salt of sorrel) with freshly precipitated antimonious oxide, and filtering the mixture whilst hot. On cooling, potassio-antimonic oxalate crystallises out. This preparation is sold at a moderate price as a substitute for tartar emetic in fixing tannin colours. D. B.

**Fixing Perthiocyanogen in Printing.** By H. SCHMID (*Dingl. polyt. J.*, **251**, 41—44).—The fact that thiocyanic acid and its salts

under the influence of oxidising agents yields yellow insoluble perthiocyanogen,  $C_3HN_3S_3$ , has long been known. Prochoroff of Moscow found that perthiocyanogen may be employed as a colouring matter, and has patented the preparation of this compound under the name of "canariu." Potassium thiocyanate,  $KCNS$ , is oxidised by potassium chlorate in the presence of hydrochloric and sulphuric acids. Bromine acts in a similar manner. The yield of colouring matter is about 40 per cent. of the weight of potassium thiocyanate employed. Canarin appears as an orange-yellow heavy powder, insoluble in water, alcohol, and ether, but soluble in strong sulphuric acid and in caustic leys. Prochoroff recommends this dye for printing wool, but makes no mention as to its application in calico-printing. Owing to its insolubility in the ordinary reagents, the only method of applying perthiocyanogen in cotton-printing is to produce it within the fibre. After making a number of trials, the author found that the best results were obtained when the printing was done with the following mixture:—

280 parts of thickening agent,  
5–15 parts of solution of vanadious chloride,  
100 parts of crystallised aluminium thiocyanate,  
100 parts of aluminium chlorate,  $40^{\circ}$  B.

The solution of aluminium chlorate is prepared by mixing 7900 grams crystallised barium chloride dissolved in 8 litres of water with a solution of crystallised aluminium sulphate in 5.5 litres of hot water. The solution of vanadium is obtained by dissolving 20 grams of ammonium metavanadate in 100 grams of hydrochloric acid and 200 of water, and reducing the solution by means of 30 c.c. of commercial sodium bisulphite. The mixture is warmed, and when solution is complete and a blue colour has appeared, it is made up to 20 litres with water: 1 litre contains 1 gram ammonium vanadate, and is therefore the same as the solution employed in the production of aniline black. The new yellow dye rapidly develops in the oxidation or drying chambers, and with the same facility as aniline black. It gives a brilliant yellow colour without weakening the fabric. Perthiocyanogen yellow is remarkable for its great stability. Neither concentrated acids nor alkalis act on it, and its tint is merely rendered lighter by nitric acid. It is altered slowly by air and light, whilst chloride of lime and boiling soap solution have no action on it. It, moreover, has the property of acting as a mordant to the aniline colours, such as methylene-blue, aniline-green, red, violet, &c. This reaction cannot be attributed to the presence of sulphur in the fibre, as it still takes place after the sulphur has been extracted. Neither can it be due to the formation of hydrocellulose, since the fixation of the aniline colours takes place when the yellow dye has formed, whereas the rotting of the fabric due to the formation of hydrocellulose was observed in the blank spaces of the pattern. Wool cannot be printed with the above mixture.

D. B.

**Preparation and Dyeing of China Grass.** (*Dingl. polyt. J.*, 251, 135–140.)—Owing to the large amount of pectinic substances



contained in China grass, it cannot be subjected to the steeping processes practised with hemp and flax, as the resulting fermentation of the pectin would destroy the texture. Hence the separation of the bast from the woody constituents must be effected by mechanical means.

The machines employed for the scutching operation separate the bast from the stem, and simultaneously remove the thin coloured upper skin from the bast. After this treatment the fibres which are still held together by the intercellular substances are separated individually by chemical means. The retting is effected by an immersion for 24 hours in warm water, boiling twice in soda-ley of  $2^{\circ}$  to  $3^{\circ}$  B. under pressure and washing. The strength of the fibres is not weakened by this treatment. The spinning is then commenced, and in some cases the fibres are bleached before spinning. To increase their lustre and elasticity, the fibres may be passed through a bath of glycerol or oil. The length of the fibre of China grass is from 6 to 25 cm. It is therefore the longest of all bast fibres. Its density is between that of flax and hemp, and its tearing length equal to 20 km. The distinctive property is its lustre.

China grass, like cotton, has little or no attraction for dyes, hence the methods in vogue for cotton are applicable also to the dyeing of China grass. The dyeing is, however, attended with more difficulty, inasmuch as its success depends on the maintenance of the lustre, smoothness and strength, which characterises the China grass fibre. Mineral colours, such as chrome-yellow and orange, destroy the silky lustre. The yellow dye obtained with cadmium sulphide, however, does not act on the fibre in this way. Alizarin mordanted with Turkey-red oil destroys the lustre, whilst aniline colours fixed with the same mordant, retain the silky appearance. Rosaniline-derivatives and the azo-colouring matters give good colours.

In conclusion, it is stated that the silky appearance which the China grass fibre possesses is not removed when it is dyed immediately after retting and before spinning. D. B.

**Preparation of Blue Dye-stuffs.** (*Dingl. polyt. J.*, 251, 240.)—Ochler obtains blue dyes from nitroso-derivatives of dimethyl-, diethyl-, or ethylmethyl-aniline, by treating their solutions in concentrated sulphuric acid or phosphoric acid with sulphuretted hydrogen gas or metallic sulphides.

Mülhauser prepares toluene-blue and anisoil-blue by treating the sulphonic acids of the amidazo-derivatives of substituted toluene and anisoil with sulphuretted hydrogen, and subsequently oxidising the sulphuretted leuco-compounds.

Lembach and Schleicher obtain a blue colouring matter by the reduction of diethylanilineazobenzene-parasulphonic acid with zinc-dust and ammonia, and subsequent oxidation with ferric chloride in the presence of sulphuretted hydrogen. D. B.

**Process for Preparing Dye-stuffs from Pyridine and Quinoline Bases.** By E. JACOBSEN (*Dingl. polyt. J.*, 250, 466—469).—By heating phthalic anhydride with pyridine and quinoline bases,

yellow condensation-products are formed. Yellow colouring matters are obtained with pyridine, picoline, the pyridine bases from coal-tar boiling between  $130^{\circ}$  and  $230^{\circ}$ , and the quinoline bases from coal-tar boiling between  $230^{\circ}$  and  $310^{\circ}$ . Quinaldine discovered by Doebner and Miller, and its homologues obtained by treating toluidine or xylidine with paraldehyde and dehydrating agents, and naphthaquin-aldine obtained from naphthylamine give similar dye-stuffs when subjected to the action of phthalic anhydride.

For the preparation of the dyes, 1 mol. phthalic anhydride is heated at  $200\text{--}250^{\circ}$  with 2 mols. of the respective pyridine or quinoline base and 1 mol. zinc chloride, and the resulting colouring matter is converted into the soluble sulphonic acid. Similar dye-stuffs are obtained if nitrophthalic acid or phthalimide is used instead of phthalic anhydride.

For the preparation of red colouring matters by the action of benzotrichloride on pyridine and quinoline bases, benzylene chloride or bromide, or benzylene chlorobromide may be employed in the place of the trichloride. Whereas most tertiary aromatic amines when treated with benzylene chloride give colourless compounds, the pyridine and quinoline bases produce dye-stuffs, which, although analogous in shade, are not identical with the reds yielded by benzotrichloride, differing in solubility and crystalline form.

The author claims as novelty the preparation of colouring matters by the action of quinoline, toluquinoline, or dimethylquinoline with additions of quinaldine, methylquinaldine, or dimethylquinaldine on benzotrichloride, benzylene chloride, &c. By treating coal-tar quinoline or synthetical quinoline with nascent hydrogen, hydroquinoline is obtained, which yields green dyes with benzotrichloride.

D. B.

**Process for Finishing Silken Goods with Amber.** By O. THÜMMEL (*Dingl. polyt. J.*, 250, 556).—One part of amber is dissolved in two parts of chloroform, and the solution is put on silken articles with a sponge or brush. The goods are then placed in a drying chamber, when the chloroform is recovered, and the articles dried. By this treatment the silk is said to acquire a peculiar softness and elasticity.

D. B.

**Method of Imparting the Appearance of Silk to Vegetable Fibres.** (*Dingl. polyt. J.*, 250, 476).—Gedge has recently patented a process for bleaching vegetable fibres and animalising them in order to render them better able to receive colours, and to give them the appearance of silk. The bleaching consists in a successive treatment with soda-ley, hydrochloric acid, and sodium hypochlorite. The animalising is effected by steeping the material in a solution of sugar, drying, and subjecting it to the action of a mixture of nitric and sulphuric acids, whereby the sugar is converted into nitroglucose, and the cellulose into dinitrocellulose.

It is said that the application of nitroglucose is not novel, as it was patented by Bonneville in 1881.

D. B.

**Presence of Tin in Preserved Food.** By E. UNGER (*Dingl. polyt. J.*, **251**, 192).—The author found that asparagus preserved in tinned boxes contained 0.019 to 0.033 per cent. tin near the sides, and from 0.021 to 0.033 per cent. in the centre of the boxes. The tin was present in the form of a proto-salt. The acid juice of pressed apricots and strawberries was found to be free from tin, whilst the fruit contained this metal. 100 grams of apricots gave 0.0185 per cent. tin, and 76.5 grams of strawberries 0.0175 per cent. D. B.

**Methods employed by Fishermen for "Barking," and in other ways preserving Nets and Sails.** By F. H. STORER (*Amer. Chem. J.*, **5**, 440—455).—On several foggy coasts the men annually "bark" their sails and nets to colour them and protect them from mildew. Oak-bark is boiled in water, and the nets are then kneaded and allowed to stand about two days, after which they are dried. Catechu is now, however, principally used instead of oak-bark. By the use of walnut-bark, *Chelidonium majus*, or young wheat plants, a "dead-leaf" colour, a dirty-orange or a green tint is imparted. In Nova Scotia, the bark of fir and spruce trees is employed, no mordant or fixing agent of any kind being employed. At Yarmouth, the nets are tanned in the beginning to preserve them from rotting, and the process is repeated at the close of the fishery to cleanse them thoroughly. A manufacturing firm in Boston fixes the catechu with potassium dichromate. An alkali—as soft soap—is also used in conjunction with bark; the alkali assists the oxidation and formation of colouring matter, and the oil probably serves much the same purpose as the emulsion of oil and alkali used in Turkey-red dyeing. In other localities, the fishermen use a mixture of bark, tar, and oil; and again others rub into the sail a mixture of tar and oil only. The sizing in new cloth is very liable to induce mildew; old sails are said to be comparatively exempt from mildew. H. B.

**Process for Preparing Hop Extract.** By W. S. FORSTER (*Dingl. polyt. J.*, **251**, 288).—The author distils hops by means of steam and recovers the ethereal oils. The residue is extracted with carbon bisulphide, and the extract, after expelling the carbon bisulphide, is neutralised with soda and evaporated in a vacuum. It is then treated with alcohol, filtered, and the residue dissolved in ether. From this solution, the lupulin is separated in the form of an alkaline salt by the addition of potash or soda. After treatment with carbon bisulphide, the hops are distilled with steam to remove the bisulphide; the tannin is then extracted with boiling water and the extract evaporated. In brewing with these substances, the tannin and lupulin extracts are added to the beer worts before boiling; whilst the hop oil is added after boiling, immediately before the commencement of the fermentation. D. B.

## General and Physical Chemistry.

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**Spark-spectra Emitted by Metallic Elements under Varying Conditions.** By E. WIEDEMANN (*Chem. News*, 49, 117).—In a recent paper (this vol., 137), Hartley stated that the short lines in some arc-spectra are lengthened by moistening the electrodes with water; and, moreover, it is suggested that this phenomenon is due to the cooling action of the water on the negative electrode, since heating the electrodes produces a reverse result. The author of the present note takes exception to this explanation, and offers the following:—When the electrodes are moistened, the discharge produces oxygen and hydrogen gases, which recombine at some distance from the electrode with great development of heat, consequently increasing the temperature of the metallic vapours, and also the length of the lines. By directly heating the electrodes, however, the potential available for the production of spark is lowered, with the result that the amount of matter dispersed at each discharge is diminished, as well as the temperature of the spark, the ultimate effect being shortened lines in the spectrum.

D. A. L.

**Spectroscopic Examination of Vapours Evolved on Heating Iron, &c., at Atmospheric Pressure.** By J. PERRY (*Chem. News*, 49, 241—242).—It is an accepted fact that most metals when heated to high temperatures, give off fumes of the metals. With iron, however, even in the Bessemer converter, no iron has been detected by the spectroscope in the fumes given off. The author shows that even when easily volatile metals are heated, no spectroscopic indication of them is given in a flame without the electric spark is passed through it simultaneously. By subjecting several substances to such treatment, the following results have been obtained.

When heated in a crucible over a blowpipe, aluminium is volatile; thallium, copper, potassium, sodium, are easily volatile, and give spectra in flame and spark. The following, of which arsenic, cadmium, zinc, and antimony are easily volatile, and bismuth, tin, lead, and manganese are so with difficulty, give spectra with spark only. Silver, chromium and gold are not volatile, but give the copper spectrum with spark. Selenium and tellurium give spectra requiring further investigation. By slightly heating either phosphorus or sulphur on a hot iron plate just below the spark, good spectra of these substances are obtained.

Spiegeleisen, when heated in a crucible, evolves a fume in which zinc, copper, manganese, calcium and magnesium (?) were detected. In a similar manner, Bessemer pig evolved copper, manganese, calcium, lead or arsenic; whilst when burnt at a low red heat in a stream of oxygen, in addition to the above a carbon spectrum was observed. Spanish iron ore reduced with charcoal in a crucible at a temperature sufficient to fuse the metal, gave zinc, copper, and manganese. When the dry chlorides, obtained by treating Spanish ore with hydrochloric

acid, are gradually heated in the blowpipe, copper, zinc, calcium, barium, lead, silver, and manganese lines are detected successively in the vapours. At the highest temperature, iron lines appear. In the same way, when spiegeleisen and steel or iron filings are treated with hydrochloric acid, or mixed with ammonium chloride and heated, the various substances volatilise much more easily and give bright successive spectra. Heated in a glass tube four inches long, the chlorides from steel gave vapours at the top of the tube in which were detected calcium, copper, and then manganese, finally only calcium and copper were observed; copper was detected in the vapour at the top of a 20-inch glass tube, at the bottom of which copper and ammonium chlorides were heated. Copper was evolved from all the metals tested. Lithium, strontium, calcium, copper, zinc, barium and magnesium chlorides give spectra when volatilised in an ordinary spirit lamp.

D. A. L.

**A Probable Cause of the Difference between the Observed Electromotive Force of Galvanic Couples and that Calculated from Thermochemical Data.** By G. CHAPERON (*Compt. rend.*, 98, 729—732).—Amongst galvanic couples which have an actual electromotive force considerably different from that calculated from thermochemical data, there are several which seem to exhibit phenomena due to the polarisation of the dissolved metal, and although these couples have a positive electrode which cannot polarise, they yield a current, the electromotive force of which falls very rapidly to zero. The author has determined the E.M.F. of several couples of this kind, and finds that they constitute systems which are polarisable up to the point of decomposition of the electrolyte into its elements, the difference of potential between the two electrodes increasing between zero and the point of electrolysis, and even beyond the latter, in accordance with an uninterrupted law. If  $TmR$ , and  $TmH$ , represent the work or electric energy corresponding, at a given temperature and pressure, with the absorption or restitution of the elements  $R$  and  $H$  of an electrolyte, by an electrode of the polarisable metal  $m$ , then  $TmR$  and  $TmH$  are not constant, but vary between very wide limits, diminishing as the proportion of  $R$  and  $H$  absorbed increases. It follows that the chemical work corresponding with the electric energy given back by the two polarised electrodes will generally be—

$$TRH - TmR - TmH,$$

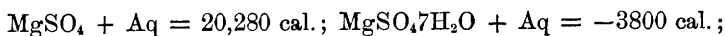
where  $TRH$  is the energy of formation of the electrolyte. When polarisation follows an uninterrupted law, this value of the chemical energy will vary from  $TRH$  to zero, between the point of electrolysis and the state of neutrality of the electrodes which is represented by the equation—

$$TRH - TmR - TmH = 0.$$

Between the same limits,  $TmR$  and  $TmH$  will vary from zero to two positive values, each of which will, at the limit, be smaller than  $TRH$ , and it is the value of  $TmR$  satisfying equation (1) which ought to be used instead of the heat of combination in calculating the theoretical E.M.F.

C. H. B.

**Heat of Hydration of Salts.** By S. U. PICKERING (*Chem. News*, 49, 216).—It is pointed out, that in calculating the heat of hydration of a salt by taking the algebraic difference between the heat of solution of the anhydrous salt and that of the hydrated salt, the heat evolved by the conversion of a certain quantity of liquid water into solid water of crystallisation is not correctly accounted for. For instance, Thomsen's numbers for magnesium sulphate are:—

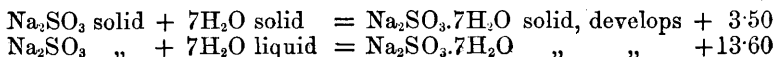


whence he deduces  $\text{MgSO}_4 + 7\text{H}_2\text{O} = 24,080 \text{ cal.}$ ; but the solidification of  $7\text{H}_2\text{O} = 10,010 \text{ cal.}$ , hence the actual heat due to the chemical action,  $\text{MgSO}_4 + 7\text{H}_2\text{O}$ , is only  $14,070 \text{ cal.}$  Such being the case, it is evident that similar corrections are required in other instances.

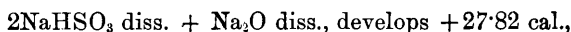
D. A. L.

**Normal and Acid Sodium Sulphites.** By DE FORCRAND (*Compt. rend.*, 98, 738—741).—Normal sodium sulphite was prepared by saturating a known weight of sodium carbonate with sulphurous acid, adding an equal weight of the carbonate, and crystallising in an atmosphere of dry nitrogen. The salt crystallises with  $7\text{H}_2\text{O}$ , all of which is given off at  $150^\circ$ . The author was unable to obtain the decahydrate described by Muspratt. The heat of solution of the hydrated salt  $\text{Na}_2\text{SO}_3 + 7\text{H}_2\text{O}$  at  $+10^\circ$  is  $-11.1 \text{ cal.}$ , and that of the anhydrous salt  $+2.5 \text{ cal.}$ , from which it follows that—

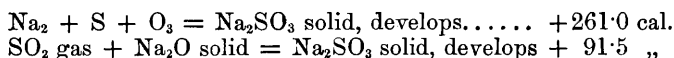
Cal.



It is also found that—



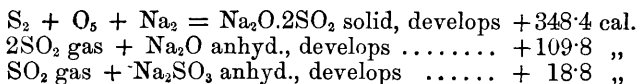
and hence it follows that—



A solution of the normal sulphite is partially decomposed by hydrochloric acid, the base dividing itself between the two acids with formation of chloride, and acid sulphite, in a manner exactly similar to that observed by Berthelot in the case of potassium sulphite.

When a solution of sodium carbonate is saturated with sulphurous acid and allowed to evaporate slowly in an atmosphere of sulphurous anhydride, sodium metasulphite,  $\text{Na}_2\text{O} \cdot 2\text{SO}_2$ , separates in large anhydrous crystals which do not alter when exposed to the air. The author was unable to obtain any hydrates of this salt. The heat of solution of the metasulphite at  $10^\circ$  is  $-5.24 \text{ cal.}$ , and when the solution is immediately treated with an equivalent of sodium hydroxide, there is a development of heat  $= +28.2 \text{ cal.}$  The mean result of several determinations of the heat developed by the action of an equivalent of soda on the metasulphite is  $+2.83 \text{ cal.}$  In the experiments described above, it was found that the action of an equivalent of soda on a solution of the acid sulphite formed at the same instant is  $+27.82 \text{ cal.}$  The difference between these numbers is so small,

that it cannot be supposed that the metaspulphite undergoes any change on solution. It follows that the true sodium hydrogen sulphite does not exist in solution, or rather, is immediately converted into the metaspulphite. The various determinations yield the following values:—



A comparison of these results with those of Berthelot and of Sabatier, shows that the heat developed by the combination of oxygen in different proportions with the various sodium sulphites is practically the same as that developed by the combination of the same amount of oxygen with the corresponding potassium sulphides.

C. H. B.

**Scales of Temperature and Molecular Weights.** By BERTHELOT (*Compt. rend.*, **98**, 952—956).—A summary of recent results respecting the density of the halogens at high temperatures, and the variations in the specific heats of elementary gases at high temperatures.

C. H. B.

**Relative Rapidity of Combustion of Explosive Gaseous Mixtures.** By BERTHELOT and VIEILLE (*Compt. rend.*, **98**, 646—651).—The maximum pressure observed when a mixture of gases is exploded in a vessel of given capacity is always less than it would be if the system retained the whole of the heat developed by the combustion, the loss of heat being due to contact with the walls of the explosion-vessel and to radiation. The difference is greater the smaller the vessel, or in other words, the smaller the mass of gas with respect to the vessel in which it is contained, and it is also greater the slower the rate of combustion. The rapidity of combustion is very variable, and is intermediate between the rapidity of detonation and that of ordinary combustion. In the experiments described in this paper, three explosion-vessels of different capacities and shapes were employed.

As a rule, the time required for the development of the maximum pressure is longer the greater the capacity of the explosion-vessel and the greater the distance between the point of inflammation and the pressure-piston. With carbonic oxide, the time required is greater than with hydrogen, whilst in the case of cyanogen and of hydrocarbons rich in hydrogen, the time is practically the same as in the case of hydrogen alone, and agrees with the calculated ratios of the velocity of the explosive waves. It is, in fact, the velocity of translation of the molecules which governs the phenomenon. When nitrous oxide is used instead of oxygen, the rapidity of combustion is diminished.

The absolute rapidity of combustion is very difficult to estimate, but assuming that the flame reaches the piston at the moment when the maximum pressure is developed, the velocity of combustion is about 100 metres per second for hydrogen, 8 metres for carbonic

oxide, 70 metres for cyanogen. When nitrous oxide is employed, the velocity of combustion of hydrogen is reduced to one-half, and that of cyanogen to one-third.

There is no evidence that the combustion of cyanogen takes place in two stages, but incomplete combustion of the gas is more rapid than complete combustion, probably because in the latter case there is partial dissociation.

The rate of combustion is diminished by the presence of an excess of one of the combustible gases, and also by the presence of an inert gas, but to a much greater extent by the presence of an excess of one of the gases which are produced by the combustion. An inert gas retards combustion partly by lowering the temperature and thus diminishing the velocity of the molecules, and partly by diminishing the number of effective encounters between the molecules which can act on one another.

In the case of so-called isomeric mixtures, the rate of combustion is lowest in the less condensed systems, which are also those which develop the smallest amounts of heat.

When two combustible gases are mixed, the rapidity of combustion of the mixture is never the mean between its constituents, but each gas appears to burn separately with its own proper rapidity, and consequently the maximum pressure observed does not correspond with a uniform state of combination of the system. When carbonic oxide and hydrogen are exploded separately with oxygen, the pressures produced are practically the same, viz., 10.1 and 9.9 atmospheres respectively, whilst with a mixture of equal volumes of the two gases, the maximum pressure developed is 8.7 atmospheres. Similar results are obtained with mixtures of hydrogen and ethylene, and in both cases it would seem that the hydrogen is the first to burn.

The rate of combustion of mixtures of hydrocarbons rich in hydrogen is very similar to that of hydrogen alone, which seems to indicate that the hydrogen burns before the carbon even in cases of complete combustion. These effects play a part in establishing those temporary conditions of equilibrium which result from incomplete combustion, such as the division of oxygen between two mixed combustibles like carbonic oxide and hydrogen, or the hydrogen and carbon in hydrocarbons, or the division of hydrogen between two substances like oxygen and chlorine. During the first moments, this division depends on the relative rapidity of the combinations, and may be very different from the definite equilibrium which would be established in the same system if it were kept at a constant temperature for a sufficient length of time. A system which is suddenly cooled, as is the case with the products of detonation, does not furnish real measures of the relative attractions of its constituents, because it may present an entirely different distribution of its elements.

C. H. B.

**Influence of the Density of Explosive Gaseous Mixtures on the Pressures which they Develop.** By BERTHELOT and VIEILLE (*Compt. rend.*, 98, 705—711).—If the pressures exerted by gaseous systems to which a given amount of heat has been communicated vary in the same ratio as their densities, it will follow, independently



of all hypotheses on the laws of gases (1), that the specific heat of the system is independent of its density, *i.e.*, of the initial pressure, and depends solely on the absolute temperature, and (2), that the relative variations of the pressures at constant volume produced by the communication of a given quantity of heat is also independent of the pressure, and is solely a function of the temperature. In order to investigate this point, two methods were adopted. The first consisted in exploding similar gaseous mixtures which had previously been heated at different temperatures, whilst the second and more accurate method consisted in exploding isomeric mixtures, *i.e.*, mixtures which originally contain the same elements in different states of combination, but are all brought into exactly the same condition by the explosion. The conclusions drawn from a large number of experiments are:—

(1.) When a given quantity of heat is communicated to a given gaseous system, the variation in the pressure of the system is proportional to its density.

(2.) The specific heat of gases is independent of the density at very high temperatures as well as at 0°.

(3.) For one and the same system, the pressure increases with the quantity of heat communicated, and the specific heat also seems to increase with this quantity.

These purely experimental results confirm the generally accepted laws of gases.

C. H. B.

**Water of Crystallisation of Salts.** By T. SALZER (*Annalen*, **223**, 1—39).—In this paper, several generalisations are collected regarding the number of molecules of water of crystallisation attached to salts, examples being given to illustrate the several points brought out.

(1.) If a monobasic acid forms both neutral and acid salts with a metallic oxide, the number of molecules of water of crystallisation is increased with decrease of proportion of acid.

(2.) If a monobasic acid forms basic as well as neutral salts, the former contain a less number of molecules of water than the latter.

(3.) If a polybasic inorganic acid forms several salts, the number of molecules of water combined increases in proportion as the hydrogen-atoms are replaced. The same rule also holds good in the organic sulphonic and carboxylic acids.

(4.) The crystalline salts of aromatic derivatives, in which two negative groups, as hydroxyl, carboxyl, or the nitro-group stand in the ortho-position, contain less water of crystallisation than the corresponding para-compound. The further introduction of a halogen element does not seem to influence the result.

Further, so far as material is at hand, it would appear that salts, derived from acids containing three electronegative groups in the ortho-position to one another, contain less water of crystallisation than those of corresponding acids in which the groups are in the para-position.

Of the acids of the acetic series, it would appear that the salts of formic acid contain less water than those of acetic acid; the calcium

salts of normal butyric, valeric, caproic, cœnanthylic, and caprylic acid have only one molecule of water of crystallisation, whilst those of isobutyric, methyl- and methylethyl-acetic have five molecules.

The barium salts do not show such a regularity, which may partly be accounted for from the known variation of the water of crystallisation of barium acetate with alteration of temperature.

V. H. V.

**Decomposition of Salts by Water.** By H. LE CHATELIER (*Compt. rend.*, **98**, 675—678).—The author considers that the decomposition of a salt by water with formation of an insoluble product is not really analogous to the dissociation of gases (Ditte, *Compt. rend.*, 1872), but can be explained by the laws of chemical equilibrium in homogeneous liquid systems, taking into account, in accordance with the laws of Berthollet, the insolubility of the product. The insoluble substance which is formed does not play any part in the establishment of equilibrium, but is at once removed from the sphere of action, and equilibrium is established only between those substances which still remain in solution. In the case of the decomposition of normal mercuric sulphate (*loc. cit.*), the mercury which is not precipitated exists in solution as normal sulphate, and not as tribasic sulphate. The true conclusion to be drawn from Ditte's experiments is that "the quantity of acid necessary to prevent the decomposition of a salt increases at first with an increase in the proportion of water, but it does not increase indefinitely, and tends towards a limit." This limit may be due to the partial dissociation of the hydrates of the acid, or, in certain cases, to the comparative insolubility of the particular salt.

C. H. B.

**Curves of Solubility of Salts.** By A. ÉTARD (*Compt. rend.*, **98**, 993—996).—The author has determined the solubility of chlorides, bromides, and iodides of calcium, strontium, barium, nickel, cobalt, manganese, cadmium, zinc, magnesium, and iron (ferrous) between the freezing points of their solutions and 180°. Whether the salt employed is usually anhydrous or hydrated, its solubility between a given interval of temperature is always represented by a straight line which makes an angle with the axis of temperature. This line seems to represent the normal solubility for a certain state of equilibrium between the water and the dissolved salt, but as the temperature continues to rise, the condition of equilibrium changes, and during the greater or less interval of temperature in which this change takes place, the curve is inflected. As soon, however, as the new state of equilibrium is established, the solubility again becomes proportional to the temperature, and is represented by a straight line making a particular angle with the axis of temperature. The solubility of all the salts employed is proportional to the temperature, and is represented by a curve consisting usually of two straight lines united by a simple or sinuous curve, but in certain cases they may be two inflexions. It is conceivable that the changes of state in the solution may take place very slowly, and that a curve of perturbation only will be obtained within the limits of observation, but no case of this kind has yet been met with.

The inflections in the curve doubtless correspond with a change in the state of hydration of the salt. The curves given in the books usually extend only between  $+ 20^{\circ}$  and  $100^{\circ}$ , and that these curves are a simple curve or straight line is due to the fact that this interval includes only that part of the phenomenon in which the change in the conditions of equilibrium takes place.

C. H. B.

### Freezing Points of Solutions of Salts of Bivalent Metals.

By F. M. RAOULT (*Compt. rend.*, **98**, 1047—1049).—The author has determined the freezing points of solutions of salts of various bivalent metals and acids of different basicities, and finds that in no case is the molecular reduction of the freezing point greater than 53. It has already been shown that the molecular reduction produced by acids and by alkaline bases and salts never reaches 50. Salts, such as the acetates of lead and copper, which have a low heat of formation, are partially decomposed in solution, and produce abnormal molecular reductions. Omitting cases of this kind, the author's observations lead to the following laws:—

(1.) Normal salts of bivalent metals and monobasic acids produce a molecular reduction of the freezing point varying from 41 to 48, the mean being 45.

(2.) Normal salts of bivalent metals and bibasic acids produce a molecular reduction between 18 and 20, the mean being 20.

(3.) Whenever, in the molecule of a salt of a monobasic or bibasic acid dissolved in 100 grams of water, an atom of a bivalent metal is replaced by an equivalent quantity (2 atoms) of a monovalent metal the molecular reduction is increased by about 20.

It follows from this third law that if the molecular reductions produced by normal salts of bivalent metals and particular acids are known, the molecular reductions which will be produced by the salts of the same acids and monovalent metals can be readily calculated. The molecular reduction produced by equivalent quantities of different salts can also be calculated, and it is found that—

(4.) Double decompositions which take place without the formation of a precipitate in solutions of normal salts of univalent or bivalent metals with monobasic or bibasic acids, produce little or no change in the freezing point of the mixture.

This fourth law has been verified by numerous experiments.

C. H. B.

### Constants of Capillarity of Liquids at their Boiling Points.

By R. SCHIFF (*Annalen*, **223**, 47—106). The phenomenon of capillarity considered in relation to the atomic constitution of compounds has hitherto been slightly investigated; the only results are those of Mendeleeff (*Annalen*, **119**), who has determined the ratios of the so-called molecular cohesion  $Pa^2d$ , in which  $P$  is the molecular weight,  $a^2$  the coefficient of capillarity, and  $d$  the sp. gr. The conclusions arrived at were: (I), in an homologous series of compounds, the molecular cohesion increases with increase of molecular weight; (II), isomeric substances have approximately equal molecular cohesion; (III), the molecular cohesion of a compound is not equal to the sum of the atomic cohesions of its components. In this extensive

memoir, the constants of capillarity are determined for a large number of carbon compounds, and the relations existing between them discussed.

On account of the alteration of the capillarity-constants with temperature, their determination under strictly comparable conditions presents some difficulty. The boiling point is selected by the author, not as presenting a condition under which liquids are in precisely the same physical state, but as the most practical, and affording, as the elaborate investigations on molecular volumes have shown, a point of sufficiently approximate physical comparability, and analogous aggregation. The process of determination consists in measuring the difference of level of the given liquid in a U-tube, whose arms are of different diameter, both however being of sufficiently small calibre that the law of diameters can be assumed to be approximately correct. The U-tube is suspended in the vapour of the liquid under examination. In the course of investigation, it was observed that the differences of level of the meniscus at first increased, but finally remained constant after the air had been completely driven out of the U-tube by the vapour of the liquid.

If  $a^2$  be the capillary elevation in a tube of 1 mm. radius, H that of the narrower limb,  $H_1$  that of the wider limb,  $r$  and  $R$  their respective radii, then  $H = \frac{a^2}{r}$  and  $H_1 = \frac{a^2}{R}$ ; if then  $h$  be the difference of level of the menisci,  $a^2 = h \frac{Rr}{R-r}$ . This value for  $a^2$  must be corrected for the weight of liquid raised from the plane tangential to the lowest part of the meniscus. If the circular angle of the tube were approximately zero, and the meniscus a semicircle, then for a radius of 1 mm.  $a^2 = h + \frac{1}{3}$ , but this correction was found to be too large; whilst the correction of Frankenheim  $\frac{f}{3}$ , where  $f$  is the true height of the meniscus, was found to be too small. The author takes the arithmetical mean as affording a sufficiently approximate correction. The equation for  $a^2$  written above will take the form

$$a^2 = \frac{Rr}{R-r} \left( h + \frac{\frac{r}{3} - \frac{R}{3} + \frac{f}{3} - \frac{F}{3}}{2} \right),$$

where  $f$  and  $F$  are the true heights of the menisci in the true branches of the U-tube. Besides the capillarity constant  $a^2$ , introduced by Poisson, another  $\frac{a^2 d}{2}$  is used, which represents the weight of liquid raised through a unit length of the line of contact between the liquid and the solid surface. If  $m$  and  $v$  be the molecular weight and volume respectively, and since  $\frac{m}{d} = v$ , then  $\frac{\frac{1}{2}a^2 d}{m} = \frac{a^2}{2v} = N$ , or the relative number of molecules elevated along the line of contact between the liquid and the solid surfaces.

For better comparison these values are multiplied by 1000.

In the table below, the experimental values are given for  $a^2$ ,  $\frac{a^2 d}{2}$ , and  $N10^3$ , determined at the boiling point, and for  $a'^2$  at ordinary temperatures :—

Liquid.	$a^2$ .	$\frac{a^2 d}{2}$ .	$N10^3$ .	$a'^2$ .
Acetone, $C_3H_6O$ .....	5·189	1·947	33·6	6·389
Paraldehyde, $C_6H_{12}O_3$ .....	3·530	1·542	11·7	5·632
Diethyl acetal, $C_6H_{14}O_2$ .....	3·656	1·346	11·4	5·611
Dimethyl acetal, $C_4H_{10}O_2$ .....	4·092	1·639	18·4	5·464
Diethyl ether, $C_4H_{10}O$ .....	4·521	1·571	21·3	5·189
Ethyl formate, $C_3H_6O_2$ .....	4·528	1·976	26·8	5·562
Propyl formate, $C_4H_8O_2$ .....	4·486	1·811	20·6	5·850
Isobutyl formate, $C_5H_{10}O_2$ .....	4·149	1·615	15·8	5·871
Isoamyl formate, $C_6H_{12}O_2$ .....	4·064	1·540	13·3	6·041
Methyl acetate, $C_3H_6O_2$ .....	4·556	2·010	27·2	5·759
Ethyl acetate, $C_4H_8O_2$ .....	4·268	1·771	20·2	5·738
Propyl acetate, $C_5H_{10}O_2$ .....	4·022	1·592	15·6	5·878
Isobutyl acetate, $C_6H_{12}O_2$ .....	3·923	1·489	12·8	5·843
Isoamyl acetate, $C_7H_{14}O_2$ .....	3·720	1·381	10·6	6·054
Methyl propionate, $C_4H_8O_2$ .....	4·289	1·806	20·6	5·878
Ethyl propionate, $C_5H_{10}O_2$ .....	3·980	1·584	15·6	5·829
Propyl propionate, $C_6H_{12}O_2$ .....	3·804	1·461	12·6	6·040
Isobutyl propionate, $C_7H_{14}O_2$ .....	3·544	1·324	10·2	5·906
Isoamyl propionate, $C_8H_{16}O_2$ .....	3·459	1·262	8·8	6·152
Methyl butyrate, $C_5H_{10}O_2$ .....	4·036	1·625	15·9	5·934
Ethyl butyrate, $C_6H_{12}O_2$ .....	3·776	1·454	12·6	5·941
Propyl butyrate, $C_7H_{14}O_2$ .....	3·621	1·350	10·4	6·117
Isobutyl butyrate, $C_8H_{16}O_2$ .....	3·361	1·221	8·5	6·046
Methyl isobutyrate, $C_5H_{10}O_2$ .....	3·965	1·595	15·7	5·643
Ethyl isobutyrate, $C_6H_{12}O_2$ .....	3·692	1·418	12·3	5·717
Propyl isobutyrate, $C_7H_{14}O_2$ .....	3·544	1·319	10·2	5·906
Isobutyl isobutyrate, $C_8H_{16}O_2$ .....	3·368	—	8·5	5·821
Methyl valerate, $C_6H_{12}O_2$ .....	3·858	1·503	12·9	5·696
Ethyl valerate, $C_7H_{14}O_2$ .....	3·6·0	1·349	10·8	5·738
Propyl valerate, $C_8H_{16}O_2$ .....	3·459	1·262	8·8	5·857
Hexane, $C_6H_{14}$ .....	4·514	1·386	16·1	6·167
Diisobutyl, $C_8H_{18}$ .....	3·909	1·205	10·5	6·195
Diisoamyl, $C_{10}H_{22}$ .....	3·579	1·096	7·7	6·603
Amylene, $C_5H_8$ .....	4·852	1·542	22·2	5·738
Caprylene, $C_8H_{16}$ .....	4·080	1·286	11·5	6·701
Diallyl, $C_6H_{10}$ .....	4·627	1·504	18·3	5·935
Benzene, $C_6H_6$ .....	5·245	2·127	27·3	6·968
Toluene, $C_7H_8$ .....	4·746	1·846	20·1	6·961
Xylene (1 : 2), $C_8H_{10}$ .....	4·437	1·677	16·0	7·039
Xylene (1 : 3), $C_8H_{10}$ .....	4·437	1·679	15·9	7·039
Xylene (1 : 4), $C_8H_{10}$ .....	4·430	1·670	15·8	6·990
Ethylbenzene, $C_8H_{10}$ .....	4·495	1·710	16·2	7·102
Propylbenzene, $C_9H_{12}$ .....	4·219	1·561	13·0	7·137
Ethyltoluene (1 : 4), $C_9H_{12}$ .....	4·184	1·546	12·9	7·088
Mesitylene, $C_9H_{12}$ .....	4·085	1·506	12·6	7·032
Cymene, $C_9H_{12}$ .....	3·839	1·391	10·4	7·018
Methyl alcohol, MeOH.....	5·107	1·909	59·8	6·012
Ethyl alcohol, EtOH.....	4·782	1·765	38·4	5·956
Propyl alcohol, Pr <sup>α</sup> OH.....	4·718	1·762	29·0	6·223
Isopropyl alcohol, Pr <sup>β</sup> OH.....	4·592	1·702	28·2	5·780

Liquid.	$a^2$ .	$\frac{a^2 d}{2}$ .	N10 <sup>3</sup> .	$a^2$ .
Isobutyl alcohol, C <sub>4</sub> H <sub>9</sub> .OH .....	4·416	1·604	21·7	6·061
Isoamyl alcohol, C <sub>5</sub> H <sub>11</sub> .OH .....	4·289	1·534	17·4	6·223
Dimethyl ethyl carbinol, C <sub>5</sub> H <sub>11</sub> .OH .....	4·283	1·550	17·6	5·949
Allyl carbinol, C <sub>3</sub> H <sub>5</sub> .OH .....	5·006	1·955	33·8	6·429
Chloroform, CHCl <sub>3</sub> .....	3·150	2·210	18·6	3·874
Carbon tetrachloride, CCl <sub>4</sub> .....	2·756	2·040	13·3	3·600
Ethylene chloride, C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> .....	4·198	2·429	24·6	5·499
Ethylidene chloride, C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> .....	3·684	2·052	20·8	-
Propyl chloride, C <sub>3</sub> H <sub>7</sub> Cl .....	4·359	1·866	23·8	5·330

As regards the amount of confidence to be placed in these results, it is noticed that if the errors of sp. gr., cathetometer reading, &c., be in the same direction, then the greatest possible variation for  $a^2$  will be 0·073 or 1·75 per cent. of the mean value of the constant, and for  $N10^3 = \frac{a^2 d}{2m}$  it will be 0·45.

From the values of  $a^2$  and  $a'^2$  can be calculated the diminution of this capillarity-constant for each degree temperature; the value so obtained can be denominated the *mean depression coefficient*. This varies with the liquid, and in any series of homologous liquids diminishes with increase of molecular weight.

The table below contains some of the values for the coefficient of various liquids:—

#### Hydrocarbons.

Paraffin.	Coefficient of depression.	Aromatic.	Coefficient of depression.
Hexane.....	0·0250	Benzene .....	0·0235
Octane .....	0·0225	Toluene .....	0·0213
Decane.....	0·0193	Xylenes (3) .....	0·0192
		Propylbenzene ....	0·0189
		Cymene .....	0·0183

#### Ethereal Salts.

Ethyl formate .....	0·0211	Methyl acetate ....	0·0249
Propyl „ .....	0·0188	Ethyl „ .....	0·0213
Butyl „ .....	0·0184	Propyl „ .....	0·0193
Amyl „ .....	0·0175	Butyl „ .....	0·0181
		Amyl „ .....	0·0173

At the critical point, the phenomenon of capillarity disappears, so if the value for  $a^2$  at the boiling point be divided by the coefficient of depression, then a number is obtained, which when added to the boiling point will give that point at which  $a^2 = 0$ . The critical temperatures calculated by these means are compared with those determined experimentally by Pawlowsky, and the values are fairly concordant.

*Discussion of the Results.*—I. In isomeric liquids of the paraffinoid

series, those of higher boiling point have higher values for  $a^2$  and  $N$ ; but in isomeric liquids of the aromatic series these substances are reversed.

II. The constant of capillarity,  $a^2$ , depends on the molecular weight, on the chemical nature of the liquid, and on the method of arrangement of the constituent atoms. On comparing the values for  $10^3N$  in the above table, it is seen that the values of hexane,  $C_6H_{14}$ , hydrocarbons of formula  $C_8H_{10}$ , and of ethereal salts of formula  $C_5H_{10}O_2$  are approximately equal. The second differ from the first in containing 2 atoms carbon more and 4 hydrogen atoms less, whilst the third differs from the second in containing 3 carbon atoms less and 2 oxygen atoms more. Hence  $2C = 4H$  and  $3C = 2O$ , and also  $C = 2H$  and  $O = 3H$ . Again, the values for  $10^3N$  of dimethyl acetal and chloroform, or of amyl formate and carbon tetrachloride are approximately equal; if the carbon and oxygen atoms be determined in terms of hydrogen by the results given above, then—

Dimethyl acetate, $C_4H_{10}O_2 = 24H$		Amyl formate, $C_5H_{12}O_2 = 30H$	
and $CH = 3H$		and $C = 2H$	
<hr/>		<hr/>	
Therefore $Cl_3 = 21H$		Therefore $Cl_4 = 28H$	
$Cl = 7H$		$Cl = 7H$	

The values for  $N$  calculated according to this method are found to be practically equal to the experimentally determined values, the only two exceptions being diallyl and ethylene chloride. Or the results may be expressed in the form of a curve, in which  $y$ , the values for  $N$ , are abscissæ, and  $x$ , the ordinates, the values in terms of  $H$ ; the curve formed is a logarithmic curve, and may be expressed by the formula  $\log y = 2.8155 - 0.00728x - \log x$ . The values calculated from this curve are compared, and are found to accord with the experimental value. Further researches in this direction are promised.

V. H. V.

**Determination of Chemical Affinities.** By W. OSTWALD (*J. pr. Chem.* [2], 29, 49—57).—VI. *Solubility of Hydrogen Potassium Tartarate in Dilute Acids.*—The finely powdered material was shaken with the normal acid for several hours at  $20^\circ$ , and after filtration a portion was titrated with baryta-water. After making a correction for the amount of substance dissolved by water alone, and proportionately increasing the amounts dissolved by each acid so that the quantity dissolved by normal nitric acid became 100, the numbers in the first column were obtained: the second column contains the numbers previously found (*J. pr. Chem.* [2], 28, 493) when using methyl acetate:—

Nitric acid .....	100	96	Ethyl sulphonic acid ..	87.0	99.0
Hydrochloric acid .....	92	100	Isethionic acid .....	92.0	99.0
Hydrobromic acid .....	93	99	Benzenesulphonic acid .	91.0	99.0
Hydriodic acid .....	94	98	Formic acid .....	7.8	11.0
Sulphuric acid .....	69	74	Acetic acid .....	4.7	5.9
Methyl sulphuric acid ....	97	100	Monochloroacetic acid ..	17.0	21.0
Ethyl sulphuric acid .....	94	99	Propionic acid .....	4.2	5.5
Propyl sulphuric acid ....	90	99	Butyric acid .....	4.0	5.5

Acids decompose hydrogen potassium tartarate into tartaric acid and the potassium salt of the acid employed, the amount of decomposition depending on the strength and on the coefficient of affinity of the acid. The results are not strictly comparable, however, the presence of the acid increasing or decreasing the solubility of the products of the reaction to a small extent.

VII. *Solubility of the Sulphates of Barium, Strontium, and Calcium in Acids.*—The amount of substance dissolved was in each case determined by evaporation to dryness; a correction was made for the amount dissolved by the water alone. The results are contained in the following table:—

Strength of acid.	Hydrochloric acid.			Nitric acid.		
	BaSO <sub>4</sub> .	SrSO <sub>4</sub> .	CaSO <sub>4</sub> .	BaSO <sub>4</sub> .	SrSO <sub>4</sub> .	CaSO <sub>4</sub> .
5·0 × normal ....	0·017	0·29	—	0·048	0·73	—
2·0 × normal ....	0·055	0·96	7·61	0·084	1·46	9·27
normal ....	0·088	1·72	11·51	0·106	2·01	13·09
0·5 × normal ....	0·130	2·20	15·75	0·137	2·44	20·37
0·1 × normal ....	—	3·25	22·96	—	3·22	23·36

Strength of acid.	Monochloroacetic acid.		Formic acid.	
	SrSO <sub>4</sub> .	CaSO <sub>4</sub> .	SrSO <sub>4</sub> .	CaSO <sub>4</sub> .
5·0 × normal ....	—	—	—	—
2·0 × normal ....	—	—	—	—
normal ....	0·104	0·41	0·080	0·31
0·5 × normal ....	0·133	0·17	—	—
0·1 × normal ....	—	—	—	—

The numbers give in milligrammes the quantity of salt dissolved by 1 mgrm. equivalent of the acid when diluted to the extent indicated.

These results point in the same direction as the previous ones, viz., that strong nitric acid has a more powerful effect than strong hydrochloric acid; but with dilute acids the effect is the same, for the coefficients of affinity of these two acids are nearly equal. The ratios between the affinities of nitric, monochloroacetic, and formic acids are also much the same as those previously deduced. H. B.

**Verification of some Atomic Weights.** By C. MARIGNAC (*Ann. Chim. Phys.* [6], 1, 289—337).—The investigations on the cerite group of metals have demonstrated the advantages of the method of fractional precipitation for the separation of substances presumably homogeneous into two or more constituents. This method is adopted



more particularly by the author in this memoir for the more or less complete elimination of impurities. The stoichiometrical analysis of substances thus purified serves as a control for previous determinations of the atomic weights.

Regarding the various scales which have been proposed for the atomic weights, it is remarked that the scale with hydrogen as unity for its basis has the advantage of representing the atomic weights of the greater number, and especially the more important of the elements, by the simplest possible integers.

*Bismuth.*—The atomic weight of this element is generally taken at 208, as the result of the concordant experiments of Schneider on the oxidation of the metal by nitric acid. From analysis of the chloride, Dumas obtained the number 210.26, but slight decomposition of the chloride by frequent distillation introduces an appreciable source of error in this method. The main points of the processes described at length in this memoir are (I) the fractional precipitation of the nitrate with water; (II) the conversion of the subnitrate into oxide by ignition; (III) the reduction of a known weight of the oxide in a current of hydrogen. The mean of six experiments on different samples of the oxide was 208.6; this process, however, presents this great inconvenience, that the oxygen eliminated forms only one-tenth of the weight of the oxide, so that the smallest error in its determination by loss would involve a tenfold error in the atomic weight of the metal. Secondly, it is observed that during the process the oxide is transformed into a black powder, probably a suboxide, and after this point is reached the reduction requires a far higher temperature by which the bismuth is melted: the molten metal is then liable to retain small quantities of oxygen. A better process consists in converting a known weight of the oxide into the sulphate by solution in dilute nitric acid, and the gradual addition of sulphuric acid to the nitrate formed. The solution of the sulphate is evaporated down and ignited at a temperature below faint red heat. The mean of six determinations with three different samples of the oxide gave the value 208.16 for the atomic weight ( $S = 32.06$ ).

*Manganese.*—The atomic weight of this metal has been determined by Berzelius and Dumas from analysis of the chloride; by v. Hauer, from conversion of the sulphate into the sulphide; Dewar and Scott, from the reduction of silver permanganate. The mean of these analyses points to 55 as the probable atomic weight of the metal, although the experiments of Rawak on the conversion of the red oxide into the peroxide, and of Schneider on the analysis of the oxalate, would lead to the atomic weight 54.

The method here adopted consists in (I) the fractional precipitation of the oxalate from an aqueous solution of the nitrate; (II) in the conversion of the oxalate into the protoxide by ignition in hydrogen; and (III) in the solution of a known weight of the reduced oxide in sulphuric acid to form the sulphate. During this last process, it is impossible to prevent a little oxidation, which is revealed by a brown coloration of the solution; the amount of this oxidation is ascertained by adding a standard solution of oxalic acid to the solution of the sulphate. The solution of the sulphate is evaporated

down and ignited at a temperature below red heat. The mean of four determinations was 55.07.

*Zinc*.—The number 65 is generally adopted as the atomic weight of zinc, from the experiments of Erdmann on the conversion of the metal into the oxide by solution in nitric acid and ignition of the nitrate. Favre and Jacquelain have substituted the value 66, but their experiments are not sufficiently trustworthy.

It is here pointed out that Erdmann's experiments are inexact, owing to the persistent retention of nitrous fumes by the zinc oxide; and if the temperature be raised sufficiently high to completely eliminate them, there is always an appreciable loss in weight of the oxide. The method here adopted consists in the conversion of the oxide into the chloride by solution in hydrochloric acid, and the evaporation of this solution with potassium chloride to obtain the double zinc potassium chloride  $2KCl, ZnCl_2$ . In this salt the proportion of zinc was determined as oxide and the chlorine by silver nitrate. From the known atomic weights of chlorine, potassium, and silver, that of zinc can be deduced. The mean value of one series consisting of five experiments was 65.29, and of another series of three experiments was 65.33. The mean of this number may be taken as a sufficiently near approximation to the atomic weight of the metal, although there are involved in the process two sources of error, viz., loss of oxide of zinc during ignition, and secondly, the retention by the double chloride of small quantities of mother-liquor, more rich in zinc chloride.

*Magnesium*.—The atomic weight of magnesium has been determined by various processes, yet the numbers vary from 24 to 24.5, although the preparation of the oxide in a state of purity presents no difficulties. After quoting experiments to show that magnesia may be ignited at a high temperature without appreciable loss of weight, the author describes the details of the conversion of known weights of the oxide into the sulphate by heating with dilute sulphuric acid at a temperature slightly below boiling point. The samples of oxide operated on were obtained by the ignition of the nitrate, sulphate, and carbonate. The mean of ten very concordant experiments gave 24.38 as the atomic weight. Another series of thirteen experiments were also made by a reverse process, viz., by the conversion of known weights of the sulphate into the oxide; the mean of these latter gave 24.37 for the atomic weight. Attempts were also made to determine the proportion of magnesium and chlorine in the double potassium magnesium chloride, but the method proved unsuccessful owing to the retention of magnesium chloride by the crystals of the double salt.

V. H. V.

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## Inorganic Chemistry.

**Density and Coefficient of Expansion of Liquid Oxygen.** By K. OLSZEWSKI (*Monatsh. Chem.*, **5**, 124—126).—A long glass bulb of 1.4 c.c. capacity is fused to a thick thermometer tube connected with a Natterer's flask containing oxygen at 50 atmospheres pressure, and also with an air manometer. The bulb is immersed in liquid ethylene, whose temperature can be reduced, by aid of an air-pump, to  $-139^{\circ}$ . On opening the valve of the Natterer's flask the bulb slowly fills with liquid oxygen. At the moment the bulb is completely filled, the supply of oxygen is cut off, the temperature and pressure of the oxygen noted, and the oxygen in the bulb allowed to evaporate and measured in the gaseous state. Corrections are made for the unliquefied oxygen in the tubes. The following table gives the results of the experiments:—

Temperature of the liquid oxygen.	Volume of gaseous oxygen (at $0^{\circ}$ and 760 mm.) obtained from the liquid oxygen.	Weight of the liquid oxygen in grams.	Density of the liquid oxygen.
129.57°	737.34 c.c.	1.0577	0.7555
139.29	858.21 „	1.2304	0.8788
137.46	834.29 „	1.1961	0.8544
139.36	856.58 „	1.2280	0.8772
134.43	787.32 „	1.1287	0.8063
139.13	858.05 „	1.2300	0.8787

From these results, the coefficient of expansion for liquid oxygen = 0.01706. The temperatures were determined by a hydrogen thermometer.  
A. J. G.

**Temperature of Solidification of some Gases and Liquids.** By K. OLSZEWSKI (*Monatsh. Chem.*, **5**, 127—128).—The reduction of temperature required for these results was obtained by means of the evaporation of liquid ethylene at ordinary pressure ( $-102^{\circ}$ ); for the lower temperatures, the evaporation was accelerated by the use of an air-pump. The temperatures were taken with a hydrogen thermometer.

Chlorine at  $-102^{\circ}$  forms an orange-yellow liquid, in which yellow crystals separate; on lowering the temperature a few degrees, the whole liquid solidifies to a yellow crystalline mass.

Hydrochloric acid is a colourless liquid at  $-102^{\circ}$ ; it solidifies at  $-115.7^{\circ}$  to a white crystalline mass, and commences to melt again at  $-112.5^{\circ}$ .

Arseniuretted hydrogen is a colourless liquid at  $-102^{\circ}$ , forms a

white crystalline mass at  $-118.9^{\circ}$ , melts again at  $-113.5^{\circ}$ , and boils at  $-54.8^{\circ}$ .

Silicon fluoride solidifies to a white amorphous mass in a glass tube cooled to  $-102^{\circ}$ ; on increasing the temperature, it slowly evaporates without previous fusion.

Ethyl ether solidifies at  $-129^{\circ}$  to a white crystalline mass; it liquefies at  $-117.4^{\circ}$ .

Amyl alcohol is an oily liquid at  $102^{\circ}$ , has a buttery consistency at  $-115^{\circ}$ , and only becomes quite frozen at  $-134^{\circ}$ , when it forms a hard semitransparent amorphous mass.

A. J. G.

**Boiling Points of Oxygen, Air, Nitrogen, and Carbonic Oxide under Atmospheric Pressure.** By S. WROBLEWSKI (*Compt. rend.*, 98, 982).—The author measures low temperatures by means of the thermoelectric properties of metals, using very sensitive aperiodic galvanometers of high resistance, the apparatus being previously graduated by comparison with a large hydrogen thermometer. In this way, it is possible to measure 0.0000025 of a volt, which corresponds with a change of temperature of  $0.2^{\circ}$  at about  $-200^{\circ}$ .

The gases employed were compressed under 100 atmospheres in a metallic receiver, and then conducted into a glass tube surrounded by liquid oxygen. The oxygen was caused to evaporate by releasing the pressure, and the gas in the glass tube was thus liquefied. The glass tube was then gradually put in communication with the air, and the liquefied gas allowed to boil under atmospheric pressure.

*Oxygen*.—Boils at  $-184^{\circ}$ . The results previously obtained at different pressures were as follow:—

Pressure.	Temperature.
50.00 atmos.	$-113.0^{\circ}$ (critical point)
27.02 „	$-129.6$
25.85 „	$-131.6$
24.40 „	$-133.4$
23.18 „	$-134.8$
22.20 „	$-135.8$
1.00 „	$-184.0$

*Air*.—Boils at  $-192.2^{\circ}$ .

*Nitrogen*, obtained by the action of metallic copper on air, boils at  $193.1^{\circ}$ . The boiling point of this gas, calculated from that of air, on the assumption that the boiling point of the latter depends on its composition, is  $-194.3$ , and it is possible that the nitrogen employed contained a small quantity of oxygen. It is evident in any case that the constituents of the air do not separate on liquefaction.

*Carbonic Oxide*.—The gas employed contained about 6 per cent. of carbonic anhydride, and the mixture boiled at  $-186^{\circ}$ . Assuming that the boiling point of carbonic anhydride is  $-80^{\circ}$ , that of carbonic oxide is  $-193^{\circ}$ , or the same as that of nitrogen.

By the evaporation of these gases in a vacuum, temperatures are obtained several degrees below  $-200^{\circ}$ .

C. H. B.

**Presence of Hydrogen Peroxide and Ammonium Nitrite, and Absence of Ozone in the Products of the Combustion of Hydrogen and Hydrocarbons in Air.** By A. R. LEEDS (*Chem. News*, 49, 237—239).—With regard to the question of formation of ozone, hydrogen peroxide, and ammonium nitrate during the combustion of hydrogen, or hydrogenous substances, in air (or oxygen), many communications have been made by various authors, some supporting and some denying the production of the various substances enumerated. After reference to these, the present note contains a description of an apparatus, by means of which the author can burn purified hydrogen or hydrocarbons (coal-gas) in purified air, and collect the products without contact with anything but glass and platinum wire. It consists of a long tube, with a globular enlargement, closed at the top; at the lower end, this fits air-tight into a receiver connected by means of a glass tube and ground stoppers with the first of a series of three bottles similarly connected; these serve for the collection of the products of combustion. Air is admitted by a lateral tube at the top, the hydrogen by a similar tube connected with a platinum jet below the enlargement; combustion is started by means of spark sent through platinum wires fused in the glass; each of the wires terminates in a minute spiral, which is wholly immersed in the flame during the combustion; they are useful, as they indicate by their incandescence the existence of a flame, and also prevent its extinction. With this apparatus, ammonium nitrite and hydrogen peroxide have been detected in the products of the combustion of pure hydrogen and hydrocarbons in purified air; but ozone and ammonium nitrate were not found. In these experiments, the products of combustion were not removed speedily from the influence of the high temperatures of the flame, as was the case in all previous experiments, hence it is possible that the ozone, if formed, was decomposed by the high temperature.

D. A. L.

**Nitrogen Iodide.** By A. GUYARD (*Ann. Chim. Phys.* [6], 1, 358—412).—Nitrogen iodide in water is decomposed slowly by the action of sunlight with evolution of nitrogen; the rapidity of the change is increased by the blue and yellow rays, decreased by the violet rays. It proceeds slowly up to a certain point, at which violent explosions occur; but if a moderately concentrated solution of ammonia be substituted for water the change occurs gradually until all the nitrogen iodide is converted into ammonium peroxide and nitrogen. The equation representing the decomposition is as follows:— $3\text{N}_2\text{H}_4\text{I}_2 = \text{N}_3 + 3\text{NH}_4\text{I}_2$ , or in the presence of ammonia,  $3\text{N}_2\text{H}_4\text{I}_2 + 4\text{NH}_4\text{OH} = 6\text{NH}_4\text{I} + 2\text{N}_2 + 4\text{H}_2\text{O}$ . It is here proposed to make use of this reaction as a means for determining the chemical intensity of daylight, and several forms of apparatus are described by which the nitrogen evolved may be measured. As regards the formula for nitrogen iodide, the author considers that Meron's and Marchand's formula,  $\text{NH}_2\text{I}$ , or preferably  $\text{N}_2\text{H}_4\text{I}_2$ , is supported by the greater weight of evidence; it is thus a diiodamine. Its formation has probably been correctly represented by Odling thus:  $3\text{NH}_3 + \text{I}_2 = \text{NHI}_2 + 2\text{NH}_4\text{I}$ , although it is noticed that whatever be the quantity of

iodine used there is always some unchanged ammonia at the end of the reaction.

The process here adopted for the preparation of nitrogen iodide consists in adding a solution of ammonia to solution of iodine in potassium, sodium, or ammonium iodides (the so-called periodides). If this latter solution be added to an ammoniacal solution of a cupric oxide, there is formed a violet-green double iodide of copper and nitrogen, whose composition is probably expressed by the formula  $2\text{CuI}_2 \cdot \text{N}_2\text{H}_4\text{I}_2$ , decomposed by water to form an oxyiodide of copper,  $\text{CuO}_2\text{I}$ .

The analysis of nitrogen iodide may be effected by sodium thio-sulphate, which converts the iodine into ammonium iodide, and causes the evolution of ammonia. The proportional quantities of free ammonia, and of combined ammonia, can be determined by distillation, and the iodine by silver nitrate. Several experimental results are here adduced, which point to the reaction between the ammonia and iodine as occurring between a greater number of molecules of these substances than was suspected by Odling.

The mother-liquors from the preparation of nitrogen iodide give precipitates with soluble salts of silver, mercury and bismuth, of which the last is probably a periodide of bismuth,  $\text{Bi}_2\text{I}_4$ . It separates out in graphite-like scales, very stable when dry, but decomposed rapidly in the presence of water to form bismuth oxyiodide.

V. H. V.

**Dimorphism of Sodium Thiosulphate.** By F. PARMENTIER and L. AMAT (*Compt. rend.*, **98**, 735—738).—It is well known that if a minute crystal of the ordinary form is added to a supersaturated solution of sodium thiosulphate, the latter crystallises in short thick monoclinic prisms, and there is considerable development of heat, but the temperature never rises above  $47\cdot9^\circ$ , the melting point of the salt. If, however, very strong solutions are cooled in a freezing mixture out of contact with any particles of the ordinary salt, the thiosulphate crystallises in long slender needles, and the temperature does not rise so high as in ordinary cases, although there is still considerable development of heat. If crystals of this kind are introduced into a supersaturated solution of the salt, they bring about the formation of precisely similar crystals, but the temperature never rises above  $32^\circ$ . When fragments of the ordinary salt are introduced into a solution containing the needle-shaped crystals, the latter disappear, heat is developed, and the salt crystallises in the ordinary form. When too, an attempt is made to isolate the needles by pouring off the mother-liquor, they are always converted into the ordinary crystals. The needles can, however, be isolated in the following manner. Two flasks, one of which contains thiosulphate, are connected together by a bent tube, the apparatus being entirely closed. The whole apparatus is then heated at  $60^\circ$  in order to destroy every trace of the ordinary crystals, and the flask containing the thiosulphate is cooled in a freezing mixture. When about half the salt has crystallised in needles the mother-liquor is decanted through the tube into the other flask. The needles are then carefully melted, a few of the crystals being left intact, about half the salt is allowed to crystallise, and the

mother-liquor decanted through the tube. By several repetitions of this process a small quantity of the salt is finally obtained, crystallised in needles, and entirely free from the ordinary short prisms. As soon, however, as the needles are brought in contact with the air they change into the ordinary crystals.

The needles have exactly the same composition as the ordinary crystals, and they also appear to belong to the monoclinic system, but they melt at  $32^{\circ}$ , whereas the short prisms melt at  $47.9^{\circ}$ . Determinations of the heat of solution of the needles show that, taking Berthelot's value  $-11.6$  cal. for the heat of solution of the short prisms, the heat of transformation of the needles into the ordinary variety is  $+2.8$  cal.

When partially dehydrated thiosulphate is treated in a similar manner, reduction of temperature does not produce the same crystals, but other salts containing less water, which crystallise at a higher temperature the lower the proportion of water. These salts are always mixed with more or less mother-liquor, and when brought in contact with the ordinary variety they change into it with development of heat.

C. H. B.

**Chlorides of Lithia and Lime.** By G. LUNGE (*Annalen*, **223**, 106—110).—This paper is principally a polemic directed against Kraut's criticism of the author's results of the reaction between lithium hydroxide and chlorine (comp. Abstract, 1883, 953). It is here shown that as at ordinary temperatures, so at  $0^{\circ}$ , the point at which Kraut investigated the change, chlorine acts very slowly upon lithium hydroxide, with production of a compound containing at most 4 per cent. available chlorine. The presence of a trace of the crystalline hydrate of the hydroxide materially increased the yield.

V. H. V.

**Hydrated Aluminium Sulphate.** By P. MARGUERITE-DE LA CHARLONNY (*Ann. Chim. Phys.* [6], **1**, 425—432).—The aluminium sulphate of commerce crystallises in rather hygroscopic tablets of composition  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ . In this paper another hydrate is described of composition  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ , crystallising in orthorhombic prisms, which effloresce slowly. This latter salt, which can be more conveniently dealt with than the former, can be obtained by the decomposition of ammonium alum by heat, by recrystallisation of the crude alum of commerce or from alunite; for its preparation care must be taken to prevent its crystallisation, *en masse*, from a concentrated solution, for the salt obtained under those conditions cannot be dried without difficulty. This hydrated sulphate also occurs as an efflorescence on schistose rocks at Rio Saldana in South America.

V. H. V.

**Vapour-density of Beryllium Chloride.** By L. F. NILSON and O. PETTERSSON (*Compt. rend.*, **98**, 988—990).—The chloride was prepared by the action of dry hydrochloric acid gas on the metal in a platinum tube, and was volatilised in an atmosphere of carbonic anhydride (in which it does not dissociate below  $706^{\circ}$ ) in Schwarz's apparatus, an air thermometer being enclosed along with the latter in an iron tube in the furnace. The following results were obtained:—

Temperature . . . .	490°	520°	589°	597°	604°
Density . . . . .	6.7(?)	4.174	3.067	3.031	3.090
Temperature . . . .	686°	720°	745°	812°	
Density . . . . .	2.853	2.926	2.753	2.793	

It follows that between 686° and 812°, the molecule of beryllium chloride is represented by the formula  $\text{BeCl}_2$ , the atomic weight of Be being 9.1. The higher values obtained at lower temperatures are due to the fact that the molecule at these temperatures consists of aggregations which split up as the temperature rises. At 520°, for example, the density 4.174 corresponds with the formula  $\text{Be}_2\text{Cl}_4$ . In this respect, beryllium chloride resembles stannous chloride.

It follows from these results that in accordance with Avogadro's law, the atomic weight of beryllium is 9.1, which agrees with its place in the periodic series, but this is the first case in which the conclusion deduced from this law does not agree with that deduced by means of the law of Dulong and Petit from the determination of the specific heat.

C. H. B.

**Disintegration of Zircon.** By F. STOLBA (*Chem. News*, 49, 174).—One part of finely powdered zircon is mixed with 4 parts of a mixture of 2 of potassium borofluoride and 3 of potassium carbonate, and fused at a red heat in a platinum crucible. The molten mass is poured on a dry metal plate, and as soon as it solidifies is thrown into water to render the mass friable, and thus facilitate subsequent pulverisation. The powder is boiled out with water and filtered. The filtrate contains the greater part of the zirconium as double fluorides, and alkalis precipitate zirconium hydroxide from it. The insoluble portion is dissolved in hydrofluoric acid, the remaining zirconium being by this means converted into zirconium potassium fluoride. Zircon is also attacked by prolonged boiling with caustic alkali. Crucibles of nickel serve well for the fusion of zircon with caustic alkali.

D. A. L.

**Normal Didymium Molybdate and the Valency of Didymium.** By A. COSSA (*Compt. rend.*, 98, 990—993).—Normal didymium molybdate is obtained as an amorphous precipitate by mixing warm moderately concentrated solutions of didymium nitrate and sodium molybdate. It has the composition  $\text{DiO } 43.39$ ,  $\text{MoO}_3 \text{ } 56.47 = \text{DiMoO}_4$ . Attempts to obtain the salt in crystals by fusing didymium sulphate with sodium molybdate and chloride resulted only in the formation of mixtures of acid and basic molybdates; but by simply fusing the amorphous salt at a very high temperature, a crystalline homogeneous mass is obtained. The crystals belong to the quadratic system, and present only the octahedral faces  $b\frac{1}{2}$ , which are somewhat rounded, although very brilliant. According to Friedel, the angles are,  $b\frac{1}{2}b\frac{1}{2} 49.6^\circ$ ; terminal face,  $79.46^\circ$ ; the corresponding angles on wulfenite being  $48.25^\circ$  and  $80.2^\circ$  respectively. Crystals of a mixed didymium lead molybdate containing 28.56 per cent. of lead molybdate were obtained by fusing the amorphous precipitate formed on mixing sodium molybdate with a solution of lead and didymium nitrates. The angles of these crystals, according to Friedel, are: terminal face,



$80^{\circ} 11' 3''$ ;  $b\frac{1}{2}b\frac{1}{2}$ ,  $49.5^{\circ}$ . It is evident that didymium molybdate is strictly isomorphous with lead molybdate, and this fact confirms the conclusions drawn from the author's previous researches on didymium tungstate (Abstr., 1879, 695) that the oxide of didymium is analogous to that of lead or calcium, and has the formula  $\text{DiO}$ .

C. H. B.

**Separation of Gallium.** By L. DE BOISBAUDRAN (*Compt. rend.*, 98, 711—712).—*From Boric Acid.*—1. The solution is strongly acidified with hydrochloric acid, and the gallium precipitated as ferrocyanide. The excess of ferrocyanide is removed by means of cupric chloride, the precipitate washed with dilute hydrochloric acid, and the copper removed from the filtrate by means of hydrogen sulphide. The filtrate from the copper sulphide is evaporated over potash in a vacuum, then mixed with calcium chloride, supersaturated with ammonia, and evaporated to dryness at a gentle heat, the boric acid being estimated by Ditte's method (*Compt. rend.*, 1875, 490). The calcium borate which is thus obtained is sometimes mixed with a little ferric oxide. In this case it is dissolved in hydrochloric acid, neutralised by a mixture of potassium and sodium carbonates or hydroxides in equivalent proportions and ignited. The residue is treated with water, which leaves the ferric oxide undissolved, whilst the boric acid passes into solution, and is again treated by Ditte's method.

2. The slightly acid solution of the chloride is mixed with an excess of sodium and potassium acetates in equivalent proportions, and a suitable quantity of arsenious anhydride, and then treated with hydrogen sulphide. The arsenious sulphide carries down the gallium. A current of air is passed into the filtrate, in order to expel the greater part of the hydrogen sulphide, and the liquid is mixed with a considerable excess of potassium and sodium hydroxides in equivalent proportions, evaporated to dryness in a gold vessel, and strongly heated with exposure to air. The residue is dissolved in very dilute hydrochloric acid, and the boric acid in the solution estimated by Ditte's method. This process is especially useful for the separation of small quantities of gallium from large quantities of boric acid.

An aqueous or hydrochloric acid solution of boric acid loses no sensible trace of this substance when evaporated in a vacuum at ordinary temperatures.

C. H. B.

**A Metallic Radicle.** By P. SCHÜTZENBERGER (*Compt. rend.*, 98, 985—988).—If spongy platinum is added to four or five times its weight of tin at about  $400^{\circ}$ , combination takes place with development of heat and light, and the resulting alloy, when granulated by being poured into cold water, is somewhat less white than tin alone. When this alloy is heated, in an atmosphere of hydrogen or carbonic anhydride, with hydrochloric acid diluted with its own volume of water, hydrogen is given off, and part of the tin dissolves as stannous chloride. When the evolution of hydrogen ceases, the residue consists of very thin glistening blackish-grey lamellæ, which closely resemble graphite; these, when washed with acidulated water, and finally with pure water to remove all traces of excess of tin, and then dried,

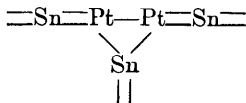
soil the fingers and leave a mark on paper. This residue consists mainly of platinum and tin, with small quantities of hydrogen and oxygen, and a considerable proportion of chlorine. The chloride could not be isolated, because it is gradually decomposed by warm water. By treating the residue with warm dilute ammonia, the whole of the combined chlorine is removed, and a hydrated oxide is obtained resembling the chloride in appearance, but with a slightly brown colour. When dried in a vacuum over sulphuric acid, it has the composition  $Pt_2Sn_3O_4H_2$ , and on reduction by hydrogen it yields a greyish-white pulverulent almost infusible alloy of the composition  $Pt_2Sn_3$ , identical with that obtained by Deville and Debray by melting 1 part of platinum with 6 parts of tin, and treating the cold alloy with hydrochloric acid. In this latter case it is probable that the large crystals in which the alloy  $Pt_2Sn_3$  was obtained, were only superficially attacked by the hydrochloric acid.

If the pulverulent alloy is heated to dull redness in oxygen, combination takes place with incandescence, and the oxide formed has the composition  $Pt_2Sn_3O_3$ . The reduction and reproduction of this oxide can be repeated any number of times.

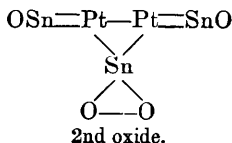
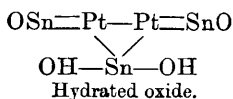
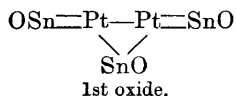
If the hydrated oxide is heated in a current of dry oxygen, water is given off, but is replaced by oxygen, and an oxide of the composition  $Pt_2Sn_3O_4$  is formed. If, however, this compound is reduced by hydrogen, and the residue reoxidised, the oxide  $Pt_2Sn_3O_3$  is alone obtained.

These stanno-platinic compounds have considerable catalytic power. They oxidise alcohol into aldehyde, and when the hydrated oxide is brought in contact with hydrogen, there is a considerable development of heat. When the pulverulent alloy  $Pt_2Sn_3$  is brought in contact with chlorine, a large amount of heat is developed, and stannous chloride volatilises.

The compound  $Pt_2Sn_3$  may be regarded as formed by the combination of a hexavalent group, consisting of two atoms of platinum  $\equiv Pt-Pt \equiv$ , with three tetravalent atoms of tin, forming a new hexavalent group,



the derivatives of which will have the constitutions



If the residue left after removing the excess of tin by dilute hydrochloric acid is subjected to prolonged treatment with concentrated hydrochloric acid, a residue is obtained, which contains less than one atom of tin, and continued action of the acid would probably remove the whole of the tin.

The solution of stannous chloride obtained by treating the alloy with dilute acid becomes yellow when exposed to the air, and contains platinum, from which it would seem that stannoplatinic chloride is not completely insoluble.

C. H. B.

**Yellow and Red Lead Monoxide.** By A. GEUTHER (*Annalen*, **219**, 56—71).—The author has prepared both modifications of lead monoxide in the pure state. The yellow variety is obtained by strongly heating lead carbonate or nitrate, if barely to the melting point as an amorphous powder, if above as a crystalline mass. It is also obtained by adding an excess of strongly diluted sodium or potassium hydroxide solution to a boiling solution of a lead salt, or by heating in a silver basin 1 part lead hydroxide with 7 parts sodium hydroxide and 14 parts water at the boiling point, until nearly all the lead hydroxide is dissolved, and slowly cooling. As the yellow variety is formed at a high temperature, it can also be obtained by strongly heating the red. The red variety is formed when lead hydroxide is heated at  $110^{\circ}$ ; also when 1 part lead hydroxide is dissolved in 5 parts potassium hydroxide, and the mixture is allowed to cool extremely slowly; lastly, the red variety may be obtained by boiling an excess of lead hydroxide in dilute caustic soda, until all the yellow which is first formed has disappeared. The yellow oxide is of a sulphur colour, forming rhombic crystals of 9.25 sp. gr. at  $15^{\circ}$ , and becomes yellowish-red on pressing and rubbing. The red oxide is of an iron- or garnet-red, according to its state of division, and forms tetragonal crystals of 9.125 sp. gr. at  $14^{\circ}$ . Both modifications can be obtained from the basic lead nitrate  $(\text{PbO})_3\text{HNO}_3$ , which is best made by slowly precipitating lead nitrate with double the necessary quantity of ammonia solution, and agitating well. At  $170^{\circ}$ , this salt loses water and is converted into  $\text{Pb}_6\text{O}_5(\text{NO}_3)_2$ . If the salt  $(\text{PbO})_3\text{HNO}_3$  is treated with pure dilute caustic soda, the yellow variety is formed, and if the second salt  $\text{Pb}_6\text{O}_5(\text{NO}_3)_2$  is similarly treated, the red variety is formed. The author therefore considers that the yellow variety must have the formula  $\text{Pb}_3\text{O}_3$  or  $(\text{Pb}_3\text{O}_3)_m$ , and the red variety the formula  $\text{Pb}_6\text{O}_6$  or  $(\text{Pb}_6\text{O}_6)_m$ , and that this polymerism affords an explanation of the dimorphic forms of lead oxide.

A solution of lead monoxide in melted potassium hydroxide rapidly absorbs oxygen, with formation of potassium salts of lead dioxide; these appear to have the formulæ  $\text{K}_2\text{O}, \text{PbO}_2$  and  $2\text{K}_2\text{O}, 3\text{PbO}_2$ ; they crystallise in hexagonal plates, and are decomposed by water.

A. B.

**Bismuthic Acid.** By C. HOFFMANN (*Annalen*, **223**, 110—136).—Potassium salts of bismuthic acid are obtained when a current of chlorine is passed into a boiling, not too concentrated, solution of potash, in which bismuth hydroxide is suspended; the resultant sub-

stance is then separated off, and the process repeated. The potassium salts have the composition  $2\text{KBiO}_3 + n\text{Bi}_2\text{O}_5$ , and are of a red to dark violet-brown shade; the more concentrated the alkali, the greater is the proportion of potassium present, but this can be removed by boiling with water or preferably by carbonic acid; in no case, however, was pure bismuthic acid obtained. These compounds, when treated with acetic acid, yield the orange bismuthyl bismuthate,  $\text{Bi}_4\text{O}_9$ , and with nitric acid the golden bismuthyl bismuthate, or bismuth dioxide,  $\text{Bi}_4\text{O}_9$  or  $\text{BiO}_2$ .

If chlorine is passed into very concentrated potash containing bismuth hydroxide, golden to red basic bismuth salts of bismuthic acid are formed; these intermediate compounds cannot be oxidised by chlorine into bismuthic acid or its derivatives, but are converted by concentrated nitric acid into bismuth dioxide. It has been stated by Bodecher that a bismuthic acid of composition  $\text{Bi}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$  is formed, when a solution of the nitrate is precipitated by potassium cyanide. As it appears improbable that a higher oxidation product should result from such a change, the experiments were repeated. It is proved that the substance formed is bismuth bisulphide,  $\text{Bi}_2\text{S}_3$ , the sulphur being derived from impurities contained in the commercial potassium cyanide.

V. H. V.

**Uranium Compounds.** By A. DITTE (*Ann. Chim. Phys.* [6], 1, 338—358).—Hydrofluoric acid converts green uranium oxide into uranyl fluoride,  $\text{UO}_2\text{F}_2$  ( $\text{U} = 240$ ), and uranium hydrogen fluoride,  $\text{UF}_6 \cdot 2\text{HF}$ , of which the latter forms crystals, decomposed by heat into uranium and hydrogen fluorides, whilst the latter is a green insoluble powder, decomposed into uranium dioxide and a volatile oxy-fluoride,  $\text{UOF}_2$ .

On melting the fluorides of the alkali-metals with the oxide  $\text{U}_3\text{O}_8$ , there are produced double fluorides of the general formula  $\text{UO}_2\text{F}_2 \cdot 2\text{MF}$ , which are crystalline, and insoluble in water; but the uranium hydrogen fluoride produces with the oxide  $\text{U}_3\text{O}_8$ , salts of the general formula  $\text{UOF}_2 \cdot 2\text{MF}$ , crystallising in well-defined forms, and soluble in water. These latter compounds may also be obtained by treating the green oxide with hydrofluoric acid, and neutralising the liquid, after separation of the black oxide, with metallic carbonates.

The chlorides of the metals of the alkalis and alkaline earths, when calcined with the green oxide, form a crystalline uranate,  $\text{UO}_3 \cdot \text{MO}$ , together with a mixture of the crystalline oxides  $\text{UO}_2$  and  $\text{U}_2\text{O}_5$ . But in the presence of a chlorate, salts of composition analogous to the dichromate  $2\text{UO}_3 \cdot \text{M}_2\text{O}$  are obtained; in the particular case of lead, the composition of the uranate is expressed by the formula  $2\text{UO}_3 \cdot \text{PbO}$ . In the original memoir, the preparation and properties of the various uranates of the alkalis and alkaline earths, together with those of magnesium and lead, are described in full. These compounds are quite insoluble in water, and, with the exception of that of lead, infusible at a white heat.

V. H. V.

## Mineralogical Chemistry.

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**Löllingite and other Minerals from Colorado.** By W. F. HILLEBRAND (*Amer. J. Sci.* [3], **27**, 349—358).—*Löllingite*.—A cobaltiferous and nickeliferous variety of löllingite is found in several mines at the base of Teocalli Mountain, Colorado. It occurs embedded in a gangue of siderite and barytes in steel-white forms, one-eighth of an inch in diameter, with a radiate structure. When treated with hydrochloric acid, the star-like forms were found to be composed of a number of flattened ellipsoids interpenetrating at a common centre. A microscopic study proved that the fundamental form is that of löllingite, showing only the prism and macrodome. These two forms are often equally developed, producing a resemblance to a low tetragonal pyramid. The angle of the prism was found to be very nearly  $122^\circ$ . An analysis of carefully isolated löllingite gave the following results:—

As.	S.	B.	Cu.	Fe.	Ca.	Ni.	Total.	Sp. gr.
71.18	0.56	0.08	0.39	22.96	4.37	0.21	99.75	7.40

This leads closely to the formula  $\text{Fe}(\text{CoNi})\text{As}(\text{S})_2$ .

Some varieties of safflorite, rhombic  $\text{CoAs}_2$ , present similar features, especially as regards the tendency to form twins of interpenetration; and, from the presence of cobalt, it might be supposed that the mineral was safflorite. The high percentage of iron, the high sp. gr., and the occurrence of a macrodome instead of a brachydome render it necessary, however, to classify it with löllingite.

*Cosalite*.—This mineral occurs in a quartz vein at the Comstock Mine, La Plata Co., Colorado, associated with iron pyrites, blende, sylvanite, and native gold. The analysis gave the following results:—

Bi.	Ag.	Cu.	Pb.	Fe.	Zn.	S.	Total.
42.97	8.43	7.50	22.49	0.70	trace	17.11	99.20

from which the formula  $2\text{RS} + \text{Bi}_2\text{S}_3$  may be deduced.

*A Mineral Probably New*.—A portion of the ore from the Missouri Mine, Park Co., Colorado, is composed of a sulpho-bismuthite of copper and silver. It occurs in a quartz gangue, associated with copper pyrites and wolfram. Small slender crystals (sp. gr. 6.31) resembling bismuthinite occur in numerous cavities. An analysis is given under I. The more compact material gave the results under II, after deducting 59.75 per cent. of gangue. A specimen (sp. gr. 2.643) from another portion of the workings gave the figures under III:—

	Bi.	Ag.	Cu.	Pb.	Fe.	Zn.	S.	Total.
I ..	60.80	0.89	15.96	—	2.13	0.10	19.94	99.82
II ..	63.42	4.09	12.65	—	0.59	0.07	18.83	99.65
III ..	62.51	9.89	6.68	2.74	0.10	0.07	17.90	99.89

After the subtraction of impurities, the atomic ratio becomes in each case nearly 3 : 4 : 15, which leads to the general formula  $3\text{RS} + 4\text{Bi}_2\text{S}_3$ .

*Hübnerite*.—This mineral was found in the Royal Albert vein, Ouray Co., Colorado. It occurs in long flattened crystals with a subvitreous lustre and brownish-black to pale yellow colour. The sp. gr. is 7.177, and the composition is as follows:—

$\text{SiO}_2$ .	$\text{Nb}_2\text{O}_5$ .	$\text{WO}_2$ .	$\text{MnO}$ .	$\text{FeO}$ .	$\text{CaO}$ .	Total.
0.62	0.05	75.50	23.40	0.24	0.13	100.02

This agrees very closely with the formula  $\text{MnWO}_4$ . B. H. B.

**Herderite.** By DES CLOIZEAUX (*Compt. rend.*, 98, 956—959).—The mineral herderite, described by Haidinger, was for a long time found only in very small quantity at Ehrenfriedersdorf, in Saxony, and on the result of blowpipe analyses by Turner and Plattner, it has been regarded as a fluophosphate of calcium and aluminium. According to Haidinger's measurements, the Ehrenfriedersdorf crystals are modified right rhombic prisms of  $115^\circ 53'$ . In 1882, somewhat large crystals were discovered at Stoneham, in Oxford Co., State of Maine, apparently identical with those from Ehrenfriedersdorf, but according to Mackintosh these crystals are calcium-beryllium-fluophosphate of the composition—

$\text{P}_2\text{O}_5$ .	$\text{CaO}$ .	$\text{BeO}$ .	F.	O.
44.31	33.21	15.76	11.32	— 4.76 = 99.84

The alumina reported by Plattner and Turner as present in the Ehrenfriedersdorf crystals may really be beryllia, but the specimens are too small and too valuable to be used for analysis. The author has however made a careful optical examination of specimens from both localities, and finds that the crystals from Stoneham are identical in their optical properties with those from Ehrenfriedersdorf, so that in all probability they belong to the same mineral species.

C. H. B.

**Identity of Scovillite and Rhabdophane.** By G. J. BRUSH and S. L. PENFIELD (*Amer. J. Sci.* [3], 27, 200).—The authors recently described (*Amer. J. Sci.*, 25, 459) a hydrous phosphate of the cerium and yttrium earths from Salisbury, Conn., as a new mineral, giving it the name Scovillite. They now find that it is essentially identical with rhabdophane, a Cornish mineral, of which only four specimens are known. The American mineral contains no cerium oxide, and has a larger percentage of the yttrium earths. Assuming the relation of the yttrium to the cerium earths to be 1 : 4, the theoretical composition may be calculated to be  $\text{P}_2\text{O}_5$ , 28.40;  $(\text{Y}, \text{Er})_2\text{O}_3$ , 11.12;  $(\text{La}, \text{Di})_2\text{O}_3$ , 53.28;  $\text{H}_2\text{O}$ , 7.20. This closely corresponds with the results obtained by W. N. Hartley (*Trans.*, 1882, 210, and 1884, 167) and the authors. The results calculated for comparison up to 100 are as follows:—

	P <sub>2</sub> O <sub>5</sub> .	(Y,Er) <sub>2</sub> O <sub>3</sub> + (La,Di) <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.	Total.
Rhabdophane ..	26·26	65·75	—	7·99	100·00
Scovillite.....	29·10	9·93	53·82	0·29	6·86

B. H. B.

**Composition of Idocrase.** By P. JANNASCH (*Jahrb. f. Min.*, 1884, 1, Mem., 269—270).—In continuation of his investigations to determine the chemical nature of idocrase (Abstr., 1883, 1067), the author notes that fluorine is a very constant constituent. TiO<sub>2</sub> seems to be still more frequent, and he has now discovered B<sub>2</sub>O<sub>3</sub> in the idocrase from the River Wilui, in Siberia. An analysis of this mineral, the so-called wiluite, gave the following results:—

SiO <sub>2</sub> .	TiO <sub>2</sub> .	B <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.
36·17	1·30	2·81	12·23	2·18	1·49	0·15
CaO.	MgO.	H <sub>2</sub> O.	F.	Na <sub>2</sub> O.	Total.	
35·81	6·05	0·72	0·22	0·45	99·58	

B. H. B.

**White Garnet from Wakefield, Canada.** By G. F. KUNZ (*Amer. J. Sci.* [3], 27, 306).—Some remarkable white garnets have been found at Wakefield. They occur in a vein in crystalline magnesian limestone. The crystals vary in size from 1 mm. to 80 mm. in diameter. Associated with the garnet are crystals of pyrrhotine and white pyroxene. An analysis gave the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	CaO.	MgO.	Total.	Sp. gr.
38·80	22·66	1·75	0·30	35·00	0·68	99·19	3·60

B. H. B.

**Action of Heat on Heulandite.** By E. MALLARD (*Jahrb. f. Min.*, 1884, 1, Ref., 312—313).—When examined under the microscope at an increasing temperature, heulandite shows no such alterations as are, for example, displayed by boracite. If a plate of heulandite is heated to 150°, the refractive power alters but slowly; white patches appear at the edges and gradually fill up the plate, showing a change which can evidently be due only to a loss of water. If a plate altered in this way be placed in Canada balsam the changed condition may be retained; but if it remains exposed to the air, it absorbs moisture and returns slowly to its original state. If the plate is laid in water, the change is effected rapidly. When heated to 180°, the plate breaks into pieces, and does not return to its original condition. The author explains these phenomena as follows: Heulandite contains 5 mols. H<sub>2</sub>O, two of which belong to its constitution. If the latter, which are set free only at a high temperature, are driven off, the molecular construction is destroyed. This is not the case when the 3 mols. H<sub>2</sub>O, set free at a low temperature, are released. They then separate from the substance by a purely physical process, like water from a sponge. After the expulsion they may be taken up again and distributed throughout like the colouring matter in crystals. The successive expulsion of these 3 mols. H<sub>2</sub>O is accompanied by a change of the inclination of the optical axis, the position of the axial plane, &c.

The author finds that beaumontite, brewsterite, chabasite, and desmin, minerals with a high percentage of water, behave like heulandite; while heat appears to have no action on mesotype and analcime.

B. H. B.

**The Olivine of the Melitite-basalt of Hochbohl.** By A. STELZNER (*Jahrb. f. Min.*, 1884, 1, Ref., 270—271).—An error having been discovered in the analysis of the olivine from the melitite-basalt of Hochbohl (Abstr., 1883, 719), the author has caused another analysis to be made, which gave the following results:—

SiO <sub>2</sub> .	MgO.	FeO.	Ni.	Insol. residue.	Total.
39.12	44.80	13.16	trace	3.00	100.08

B. H. B.

**Zeolites in the Dolerites of Chaux-de-Bergonne (Puy-de-Dôme).** By F. GONNARD (*Compt. rend.*, 98, 1067—1068).—In addition to the phacolite, mesolite, and christianite already known to exist in the dolerites of the district of Chaux-de-Bergonne, the author has found gismondite in small white octahedra, apparently macled, and phillipsite in small crystals in cruciform macles.

C. H. B.

**The Freiberg Gneiss.** By A. STELZNER (*Jahrb. f. Min.*, 1884, 1, Mem., 271—275).—The author has for some time been engaged in a petrographic examination of the Freiberg gneiss in order to test the correctness of Sanberger's theory of the formation of ore-deposits by lateral secretion. In the course of his investigations, he has discovered that the gneiss is rich in columnar crystals of zircon, accompanied by tourmaline, garnet, and apatite. In the undecomposed gneiss from the Himmelfahrt Mine, magnetic pyrites, iron pyrites, and probably some arsenical pyrites were found, the qualitative analysis of the non-magnetic pyrites giving Fe, Ni, Co, and As. The principal minerals of the decomposed gneiss are quartz, felspar, and mica. The latter is, partially or entirely, converted into potash-mica and forms, in hexagonal plates and small globular aggregates, the principal mass of the altered gneiss. This secondary mica has been analysed with the remarkable result that it contains, together with 0.41 TiO<sub>2</sub>, 0.54 SnO<sub>2</sub> as chemical constituents.

Other products of the decomposition of the gneiss are rutile and anatase. It is evident that these titaniferous minerals are the products of the decomposition of the brown mica of the gneiss, which often contains a large percentage of TiO<sub>2</sub>. The analysis of the anatase-holding heavier portion of the country rock of the Carl Stehende vein showed that the portion insoluble in aqua regia and hydrofluoric acid contained 11.44 per cent. SnO<sub>2</sub>, and hence the fine needles in the residue are evidently tin-ore.

With regard to the minerals constituting the undecomposed rock, the following may be mentioned: From 715 grams of gneiss from the Himmelfürst Mine were obtained, with the help of Thoulet's solution, 12.20 grams pyrites, rutile, garnet, tourmaline, zircon, and apatite; and from this 4.65 grams magnetic pyrites was extracted with the magnet. The latter gave on analysis 0.61 Ni and 0.12 Co, but no



metallic constituent. In 20 grams of the brown mica of the gneiss, traces of Ni and Co were found; whilst in the white mica 4.42 per cent. FeO and 0.03 per cent. Cu, with a little sulphur, were found. The felspar proved to be free from baryta and other abnormal constituents.

The author reserves all conclusions as to the mode of formation of the Frieberg veins for a final report to be published as soon as the analyses are completed.

B. H. B.

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## Organic Chemistry.

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**Action of Iodine Monochloride on Monobromethylene.** By L. HENRY (*Compt. rend.*, **98**, 680—682).—Monobromethylene combines slowly with iodine monochloride at the ordinary temperature, but combination is not complete until after several days, the liquid having been frequently agitated. An oily brownish liquid separates from the aqueous solution, and when decolourised with aqueous potash, dried over calcium chloride, and distilled, it yields chlorobromiodethane,  $C_2H_3ClBrI$ , a colourless liquid, which rapidly becomes brown. It has a somewhat sharp, agreeable odour, with a sweet, burning taste, and boils under the ordinary pressure at  $193$ — $195^\circ$  with partial decomposition; sp. gr. at  $0^\circ = 2.53$ . When treated with an equivalent quantity of alcoholic potash, chlorobromiodethane is instantly decomposed; potassium chloride and iodide are precipitated together in the proportion of  $3KCl$  to  $KI$ , and on adding water to the alcoholic filtrate, a heavy oily liquid is thrown down; this, when decolourised by potash, dried, and distilled, yields a small quantity of unsymmetrical chlorobromethylene,  $CH_2:CClBr$ , which boils at  $63^\circ$  and polymerises very rapidly, and a much larger quantity of unsymmetrical bromiodethylene,  $CH_2:CBRI$ , which boils at  $128$ — $130^\circ$  with partial decomposition.

It follows from these results that the product of the action of monobromethylene on iodine monochloride is a mixture of the two isomerides,  $CH_2I:CHBrCl$  and  $CHBrI.CH_2Cl$ , in the proportion of 1 mol. of the former to 3 mols. of the latter. The chlorine and the iodine both combine with the two groups  $CHBr$  and  $CH_2$ , but in unequal proportion, the chlorine combining most readily with the highly hydrogenised  $CH_2$ -group; whilst the iodine combines most readily with the  $CHBr$ -group, containing the bromine. This reaction is of the same order as that of iodine monochloride on monochlorethylene, but the proportional distribution of the haloïds is essentially different in the two cases.

Chlorobromiodethane is readily decomposed by bromine with the formation of a chlorodibromethane which, when treated with alkalis, yields the two compounds  $CH_2:CBrcI$ , boiling at  $63^\circ$ , and  $CH_2:CBBr_2$ ,

boiling at 88—90°, the latter being in much larger proportion than the former. C. H. B.

**Unsymmetrical Chloriodethylene and Bromiodethylene.** By L. HENRY (*Compt. rend.*, **98**, 741—744).—*Chloriodethylene*,  $\text{CH}_2:\text{CClI}$ , is obtained in small quantity by the action of a slight excess of alcoholic potash on chlorobromiodethane (preceding abstract). It is a colourless liquid which decomposes rapidly when exposed to light, eventually becoming deep purple. It is insoluble in water, and when freshly distilled has a slight ethereal odour, but it slowly absorbs oxygen, and after some time has the odour of acid chlorides. It boils, with partial decomposition, at 100—101° under a pressure of 759 mm.; sp. gr. 0° = 2.1431. Unlike the chlorobromo-derivative it does not readily polymerise.

*Bromiodethylene*,  $\text{CH}_2:\text{CBrI}$ , is the principal product of the action of alcoholic potash on chlorobromiodethane (*loc. cit.*). It is a colourless liquid, which rapidly becomes violet, and is insoluble in water; sp. gr. at 0° = 2.5651. It boils at 128—130° with partial decomposition, under a pressure of 764 mm.; does not readily polymerise, and absorbs oxygen somewhat more slowly than the preceding compound.

The following table gives the formulæ and boiling points of the known symmetrical and unsymmetrical di-haloïd derivatives of ethylene:—

<i>Symmetrical.</i>			<i>Unsymmetrical.</i>		
Diff.	B. p.	Diff.	B. p.	Diff.	
55° {	$\text{CHCl}:\text{CHCl} \dots$ 55°	20°	$\text{CH}_2:\text{CCl}_2 \dots$ 35°	} 55°	
	$\text{CHBr}:\text{CHBr} \dots$ 110	20	$\text{CH}_2:\text{CBr}_2 \dots$ 90—91		
	$\text{CHI}:\text{CHI} \dots$ 190				
37 {	$\text{CHCl}:\text{CHBr} \dots$ 81—82	19	$\text{CH}_2:\text{CClBr} \dots$ 63	} 37—38	
31 {	$\text{CHCl}:\text{CHI} \dots$ 119	19	$\text{CH}_2:\text{CClI} \dots$ 100—101		
	$\text{CHBr}:\text{CHI} \dots$ 150	20	$\text{CH}_2:\text{CBrI} \dots$ 128—130	} 29	
27 {	$\text{CHCl}:\text{CHCl} \dots$ 55	20	$\text{CH}_2:\text{CCl}_2 \dots$ 35		
68 {	$\text{CHCl}:\text{CHBr} \dots$ 81—82	19	$\text{CH}_2:\text{CClBr} \dots$ 63	} 28	
40 {	$\text{CHBr}:\text{CHI} \dots$ 150	20	$\text{CH}_2:\text{CBrI} \dots$ 128—130		
	$\text{CHBr}:\text{CHBr} \dots$ 110	20	$\text{CH}_2:\text{CBr}_2 \dots$ 90—91	} 40	
64 {	$\text{CHCl}:\text{CHCl} \dots$ 55	20	$\text{CH}_2:\text{CCl}_2 \dots$ 35		
	$\text{CHCl}:\text{CHI} \dots$ 119	19	$\text{CH}_2:\text{CClI} \dots$ 100—101	} 65	

The unsymmetrical derivatives, whether simple or mixed, are more volatile than the isomeric symmetrical compounds, the difference between the boiling points of the corresponding members of the two series being always 19—20°, and the difference between the boiling points of any two terms in the one series is the same as the difference between the corresponding two terms in the other series. The substitution of one haloïd for another produces the same change of boiling point in both series. If the position of the haloïds with respect to the nucleus  $\text{C}=\text{C}$  in these derivatives exerts great influence on their volatility and determines their boiling point, this position is entirely without influence on their *relative* volatility, which depends

exclusively on the nature of the haloïd, that is, on the molecular weight.

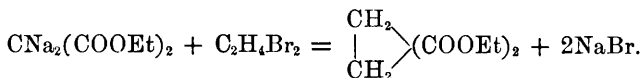
The sp. gr. of the symmetrical derivatives is, as a rule, higher than that of the corresponding unsymmetrical derivatives, as is seen in the following table:—

	Sp. gr. at 0°.
CHCl:CHI .....	2·230
CH <sub>2</sub> :CCl .....	2·140
CHBr:CHI .....	2·750
CH <sub>2</sub> :CBrI .....	2·560
CHI:CHI .....	3·303
CH <sub>2</sub> :Cl <sub>2</sub> .....	2·942

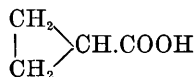
Precisely similar relations hold good in the case of the di-derivatives of ethane.

C. H. B.

**Action of Ethylene Bromide on Ethyl Malonate.** By W. H. PERKIN, Jun. (*Ber.*, 17, 54—59).—When sodium (9 grams) is dissolved in absolute alcohol (90—100 grams), and the product treated with a mixture of ethyl malonate (30 grams), and ethylene bromide (36 grams), *ethyl trimethylenedicarboxylate* is produced:



It is a colourless oil, which boils at 206—208° (720 mm.). The free acid may be obtained by saponifying it with alkali and then adding an acid; it is a crystalline substance, melting at 140—141°, and decomposing slowly at 160° with evolution of carbonic anhydride; it is extremely soluble in water, much more so than in ether. Bromine acts on it very slowly in the cold, but disappears with evolution of hydrobromic acid when heated. The silver salt,  $\text{C}_5\text{H}_4\text{O}_4\text{Ag}_2$ , forms a white precipitate, somewhat soluble in water. When trimethylenedicarboxylic acid is heated in an oil bath at 210°, carbonic anhydride is abundantly evolved, whilst *trimethylenemonocarboxylic acid*,



distils over. This is a colourless liquid, boiling at 188—190°; it has a slight odour, is somewhat soluble in water, readily in ammonia. The ammonium salt is very readily soluble, and crystallises in scales; the silver salt,  $\text{C}_4\text{H}_3\text{O}_4\text{Ag}_3$ , forms a white amorphous sparingly soluble precipitate, and when heated yields a readily volatile liquid, which is probably the anhydride of the acid. At the ordinary temperature bromine has no action on the monocarboxylic acid, but on warming it reacts with evolution of hydrobromic acid.

A. K. M.

**Synthesis of Dihydric Alcohols from Mixtures of Aldehydes.** (Preliminary Communication.) By W. FOSSEK (*Monatsh. Chem.*, 5, 119—120).—The author has previously shown that diisopropylethylene

glycol is formed by the action of alcoholic potash on isobutaldehyde; analogous glycols are obtained by the action of alcoholic potash on a mixture of equal molecular weights of isobutaldehyde and another aldehyde, or by the addition of sodium-amalgam to an alcoholic solution of such mixture. These glycols are all crystalline, distil unchanged, are insoluble in water, alcohol, and ether.

*Methylisopropylethylene glycol*,  $\text{CHMe}(\text{OH})\cdot\text{CHPr}^{\beta}\cdot\text{OH}$ , prepared from acetaldehyde and isobutaldehyde, is a thick colourless liquid, solidifying at about  $0^{\circ}$  to a compact white crystalline mass. It boils at  $204\text{--}208^{\circ}$ , has a faint agreeable odour, and a burning peppermint-like taste.

*Isobutyl-isopropylethylene glycol*,  $\text{CHBu}^{\beta}(\text{OH})\cdot\text{CHPr}^{\beta}\cdot\text{OH}$ , obtained from isovaleraldehyde and isobutaldehyde, crystallises in long needles, and melts at  $80\text{--}81^{\circ}$ .

*Phenylisopropylethylene glycol*,  $\text{CPhH}(\text{OH})\cdot\text{CPr}^{\beta}\text{H}\cdot\text{OH}$ , from benzaldehyde and isobutaldehyde, melts at  $81\text{--}82^{\circ}$ , is soluble in benzene, and has an agreeable aromatic odour.

A crystalline product (m. p.  $94^{\circ}$ ) obtained by the action of alcoholic potash on a mixture of acetone and isobutaldehyde, is also under investigation.

A. J. G.

**Action of Solutions of Cellulose on Polarised Light.** By A. LEVALLOIS (*Compt. rend.*, **98**, 732—735).—A 1 per cent. solution of purified cotton in Schweizer's ammonio-cupric reagent, has a lævoro-rotatory power for the light which passes through the ammonio-cupric liquid of about  $-20^{\circ}$ . Comparative experiments on the action of sugar on this light and on sodium light show that the deviations observed in the first case must be multiplied by 1.85, in order to render them comparable with those observed in the second. The degree of rotation is not strictly proportional to the amount of cotton dissolved, but increases somewhat more slowly than the concentration of the solution. If the solution is diluted with water or with ammonia, the rotatory power at first rapidly diminishes, but afterwards a condition of equilibrium is established, beyond which any further dilution has little effect. If the ammonio-cupric solution is prepared by dissolving precipitated cupric hydroxide in ammonia, instead of metallic copper, it dissolves a greater proportion of cellulose, and dilution with water produces different results, the curve being slightly convex towards the axis representing the deviation of the polarised ray. For the same proportion of cellulose, solutions containing increasing proportions of oxide of copper produce increasing amounts of rotation, but the relation between the two quantities has not yet been ascertained.

Flax, hemp, filter-paper, and carefully purified tunicin from *Ascidia intestinalis*, have the same rotatory power as cotton, but hydro-cellulose prepared by Girard's method is slightly less active, the rotation produced by a 1 per cent. solution being  $-19.5^{\circ}$ .

C. H. B.

**Action of Phosphorous Trichloride on Aldehydes.** By W. FOSSEK (*Monatsh. Chem.*, **5**, 121—123).—By the action of phcsphorous trichloride on propionic, isobutyric, isovaleric, and benzoic aldehydes,

and subsequent treatment with water, similar products are obtained, from which an acid containing phosphorus may be isolated in each case. These acids are crystalline, stable in air, readily soluble in water or alkalis, less soluble in alcohol, still less in ether, and nearly insoluble in benzene. They do not volatilise in a current of steam. The aqueous solutions do not give precipitates with silver nitrate until neutralised with ammonia, when white precipitates are obtained, readily soluble in nitric acid and in ammonia; the latter solution does not yield a precipitate of silver on heating. The potassium and barium salts are readily crystallisable. The acids are not decomposed by several hours' boiling with aqueous potash.

The acid,  $C_4H_{11}PO_4$ , derived from isobutaldehyde, is granulo-crystalline, and melts at  $168-169^\circ$ . The barium salt has the formula  $(C_4H_{10}PO_4)_2Ba$ .

The acid  $C_5H_{13}PO_4$ , from isovaleraldehyde, crystallises in scales, and melts at  $183-184^\circ$ . It is isomeric with the acid obtained by Guthrie (this Journal, 1856, 139) from amyl alcohol and phosphoric acid.

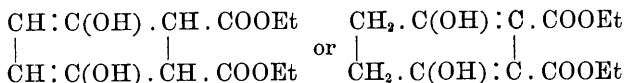
The acid from propaldehyde crystallises in scales, and melts at  $158-160^\circ$ : that from benzaldehyde is crystalline.

Phosphorous trichloride acts so violently on acetaldehyde that the products are carbonised.

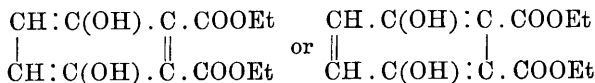
A. J. G.

**Derivatives of Ethylic Acetoacetate.** By W. WEDEL (*Annalen*, 219, 71-119).—By the action of sodium on *ethylic dibromoacetoacetate*, the author obtained a brown resinous mass, and a substance crystallising in yellow prisms, although in very small quantities; it melts at  $133^\circ$ , is insoluble in water, but soluble in hot alcohol with a strong blue fluorescence. This substance was found to be identical with Hermann's diethyl quinonehydrodicarboxylate,  $C_{12}H_{14}O_6$  (Abstr., 1882, 714), obtained by the action of bromine on diethylic succinosuccinate. By the slow action of dilute soda solution and subsequent treatment with hydrochloric acid, the free acid  $C_8H_8O_6$  was obtained in colourless crystals, which became yellow on being dried. The acid is sparingly soluble in cold, easily in hot water, and gives a deep blue coloration with ferric chloride. By acting on diethyl quinonehydrodicarboxylate with acetic chloride at  $60^\circ$  in a closed tube, a diacetyl compound,  $C_{16}H_{18}O_8$ , is formed in bright colourless crystals, insoluble in water, soluble in ether and hot alcohol, melting at  $150^\circ$ , and subliming at a higher temperature. It is decomposed by the action of dilute soda solution, with formation of quinonehydrodicarboxylic acid,  $C_6H_2\bar{A}c_2(COOEt)_2 + 4NaOH = 2EtOH + 2\bar{A}cNa + C_6H_4O_2(COONa)_2$ . In a similar way, by the action of acetic chloride on diethylic succinosuccinate at  $115-120^\circ$ , the author obtained a diacetyl compound, melting at  $168^\circ$ , and subliming at a higher temperature, but in other properties similar to the previously mentioned diacetyl compound. On account of the ease with which the above acetyl compounds are formed or decomposed by dilute caustic alkalis, the author holds that there must be an hydroxyl group in diethylic succinosuccinate, in diethyl quinonehydrodicarboxylate, and consequently also in ethylic acetoacetate, and in this his formulæ differ from those given by

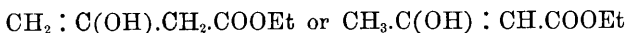
Hermann, and in the case of ethylic acetoacetate from that of Frankland and Duppa. He gives the formula



for diethylic succinosuccinate,



for diethyl quinonehydrocarboxylate, and



for ethylic acetoacetate. The author also gives various reasons for holding that the hydroxyl in the above compound has more the character of a phenol hydroxyl than an alcoholic, and on this assumption he endeavours to explain the readiness with which quinol is obtained by the distillation of diethyl quinonehydrocarboxylate.

The author failed to obtain any results by the action of sodium on ethylic tribromoacetoacetate. By acting on ethylic mono- or dibromoacetoacetate with sodium alcoholate, he obtained the same products as by the action of sodium. On preparing a bromine derivative of ethylic acetoacetate, which appeared to be a pentabromo-compound, and treating it with cupric acetate, he obtained a salt of ethylic tribromoacetoacetate,  $(\text{C}_6\text{H}_5\text{Br}_3\text{O}_3)_2\text{Cu}$ , and he considers that all bromine compounds containing more than 3 atoms of bromine are mixtures of the tribromo-compound and the perbromo-compound. Ethylic perbromoacetoacetate,  $\text{C}_6\text{Br}_{10}\text{O}_3$ , formed by the action of an excess of bromine on brominated ethylic acetoacetate for two days at  $60-80^\circ$ , is obtained as a colourless crystalline mass, melting at  $79-80^\circ$ . The copper derivative of ethylic dibromoacetoacetate,  $(\text{C}_6\text{H}_7\text{Br}_2\text{O}_3)_2\text{Cu}$ , crystallises in needles, is insoluble in water, soluble sparingly in cold, but readily in hot alcohol, and is decomposed by bases or acids, or by heating to  $100^\circ$ .

By the action of bromine on ethylic ethylacetoacetate in the cold, brominated compounds were obtained. *Ethylic monobromomethylacetoacetate*,  $\text{C}_8\text{H}_{13}\text{BrO}_3$ , is a brown strongly smelling liquid, of sp. gr. 1.354; gives a violet coloration with ferric chloride; soluble in alcohol and ether, but insoluble in water and in alcoholic solution. *Ethylic dibromomethylacetoacetate*,  $\text{C}_8\text{H}_{12}\text{Br}_2\text{O}_3$ , is a yellow fruity smelling liquid, of sp. gr. 1.635; insoluble in water, but soluble in alcohol and ether, and gives a dark wine-red colour with ferric chloride. *Ethylic tribromomethylacetoacetate*,  $\text{C}_8\text{H}_{11}\text{Br}_3\text{O}_3$ , is also a yellow liquid, of sp. gr. 1.860. By further action with bromine no definite compounds were obtained, nor did the above yield compounds with cupric acetate. At  $100^\circ$ , the monobromo-compound is decomposed into ethyl bromide, and an acid,  $\text{C}_6\text{H}_5\text{O}_3$ , or  $\text{C}_{12}\text{H}_{16}\text{O}_6$ , which the author calls ethylsuccinosuccinic acid.

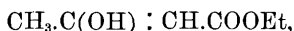
*Ethylsuccinosuccinic acid* crystallises in rhombic octahedra; melts at  $126.6^\circ$ , is soluble in water and alcohol, but is nearly insoluble in

ether and benzene, and gives a cherry-red coloration with ferric chloride. It is unchanged by boiling with baryta-water, but is completely decomposed when heated with hydrochloric acid at 120—130°.

The barium salt,  $C_{12}H_{14}O_6Ba + 2H_2O$ , forms very soluble needles; the potassium salt,  $C_{12}H_{14}O_6K_2 + H_2O$ , is obtained as a very soluble crystalline mass; the ammonium salt,  $C_{12}H_{14}O_6(NH_4)_2$ , forms needles decomposing at 80°; the sodium salt,  $C_{12}H_{14}O_6Na_2 + 2H_2O$ , is hygroscopic; the calcium salt,  $C_{12}H_{14}O_6Ca + H_2O$ , and the magnesium salt,  $C_{12}H_{14}O_6Mg + 2\frac{1}{2}H_2O$ , are crystalline powders; the zinc salt,  $C_{12}H_{14}O_6Zn + 2\frac{1}{2}H_2O$ , crystallises in tablets: the manganese salt,  $C_{12}H_{14}O_6Mn + 4H_2O$ , gives rose-coloured crystals; and the lead salt,  $C_{12}H_{14}O_6Pb$ , is less soluble. The copper salt is reduced to cuprous oxide by the action of acids. The author failed to obtain any well formed acid salts. The ethyl ether was obtained in very small quantities by the action of hydrochloric acid on an alcoholic solution of the acid.

A. B.

**Constitution of Ethylic Acetoacetate and of Benzene.** By A. GEUTHER (*Annalen*, **219**, 119—128).—The author holds that from the results of Wedel's investigation (preceding Abstract) the constitutional formula for ethylic acetoacetate must be



rather than  $CH_2 : C(OH).CH_2.COOC_2H_5$ . He also endeavours to prove the correctness of Kekulé's constitutional formula for benzene from the ease with which diethyl quinonehydrocarboxylate is formed from ethylic dibromoacetoacetate.

A. B.

**Formation of Amides from Ammonium Salts.** By N. MENSCHUTKIN (*Compt. rend.*, **98**, 1049—1052).—The ammoniacal salts were heated in bulbs at a given temperature for a definite time, and the proportion remaining unaltered was determined by titration with standard soda solution, using phenolphthaleïn as indicator. The amides are formed at temperatures above 100°; the rate of formation increases with the temperature; and, after a sufficient length of time, a maximum limit is attained. The progress of the change is precisely similar to that of etherification, as is shown by the following series of observations on the formation of acetamide from ammonium acetate at 155°:—

Time.....	1	4	8	12	24 hours
Percentage of amide formed .....	50.9	78.1	80.0	80.0	80.6
Time.....	72	144	192	216	240 hours
Percentage of amide formed .....	81.0	81.6	81.6	81.5	81.6

The initial velocity of the reaction, i.e., the proportion of amide formed in 1 hour, increases rapidly with the temperature, and depends also on the constitution of the acid. The amides of primary acids are produced much more rapidly than the amides of secondary and tertiary



acids, and this rule holds good in both the fatty and aromatic series. In homologous series, the initial velocity diminishes as the molecular weight of the acid increases.

Contrary to the law observed in etherification, the maximum limit to the formation of the amides increases considerably with an increase of temperature. This limit is not affected by the isomerism of the acid; for butyramide at  $155^{\circ}$  it is 84.13 per cent., and for isobutyramide it is 84.67 per cent. under the same conditions. For phenyl acetamide at  $155^{\circ}$  the limit is 81.5 per cent., but the formation of benzamide and anisamide take place so slowly that the maximum limit could not be ascertained. At  $125^{\circ}$ , the maximum limit to the formation of amides of the fatty acids increases with the molecular weight of the acid.

The formation of the amides from the ammoniacal salts follows the same laws as etherification, and this fact that organic compounds, in different reactions, follow the same laws, depending on their chemical constitution, is of very great importance.

C. H. B.

**Action of Chloraldehydes on Benzene in Presence of Aluminium Chloride.** By A. COMBES (*Compt. rend.*, **98**, 678—679).—When aluminium chloride is added in successive small portions to a solution of chloral in a large excess of benzene, a somewhat energetic reaction takes place even in the cold. If the liquid is heated at  $70^{\circ}$  for about an hour and a half, washed with water, and fractionated, it yields a viscous colourless liquid, which has the composition  $\text{CPhCl}_2\cdot\text{COH}\cdot\text{HCl}$ , and is the hydrochloride of the aldehyde  $\text{CPhCl}_2\cdot\text{CHO}$ . This compound is very stable, and can be distilled in a vacuum without decomposition; but when heated under ordinary pressure, it begins to boil at  $265^{\circ}$  and gradually loses hydrochloric acid, the boiling point rising to  $295^{\circ}$ . Potash in the cold removes all the hydrochloric acid without attacking the aldehyde, but, when heated, benzaldehyde and products free from chlorine are formed. The aldehyde rapidly reduces Fehling's solution and silver nitrate, and combines, although with difficulty, with sodium hydrogen sulphite. It is readily oxidised and yields the acid  $\text{CPhCl}_2\cdot\text{COOH}$ .

The prolonged action of aluminium chloride on a solution of this aldehyde in benzene yields carbon and triphenylethane,  $\text{CPh}_3\cdot\text{CH}_3$ , in yellowish-white crystals with a green fluorescence. The crystals melt at  $205^{\circ}$ .

C. H. B.

**Colouring Matters formed by the Union of Phenols with Aromatic Aldehydes.** By C. ZULKOWSKY (*Monatsh. Chem.*, **5**, 108—118).—By the action of sulphuric acid mixed with one-third of its weight of glacial acetic acid on a mixture of equal molecular weights of salicylaldehyde and phenol, a mixture of a deep-red and a colourless substance is obtained, the latter being converted into the former by oxidation in an alkaline solution. The red substance could not be obtained in a pure state; it is distinguished from aurin by not yielding a blue colouring matter when boiled with aniline.

If the phenol be employed in excess (4 mols.), the red colouring matter described by Liebermann and Schwarzer (*Abstr.*, 1876, 414)

is obtained. Analysis gives numbers agreeing better with the formula  $C_{26}O_{20}O_6$  than with Liebermann's formula  $C_{26}H_{22}O_6$ . At the same time, an ochre-yellow substance was obtained, but could not be purified sufficiently for analysis. The same substances appear to be formed by the action of parahydroxybenzaldehyde on phenol.

A. J. G.

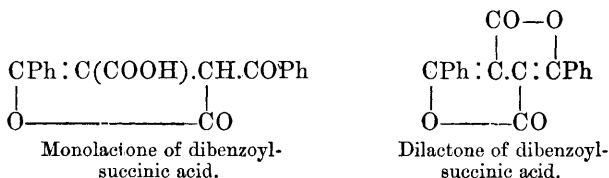
**Hipparaffin.** By K. KRAUT and Y. SCHWARTZ (*Annalen*, **223**, 40—47).—Schwartz, who isolated the so-called "hipparaffin" as a product of the oxidation of hippuric acid by lead dioxide and sulphuric acid, assigned to it the constitutional formula  $C_2H_4(NH\bar{B}z)_2$ , or ethylene-dibenzimide. This view was supported by the synthetical production from ethaldehyde and benzamide, of a substance identical in percentage composition with hipparaffin, although differing from it in melting point and solubility in sulphuric and nitric acids. The results of this paper accord with those of Schwartz as regards the physical properties of hipparaffin and its decomposition on distillation, and the non-formation of a bromo-derivative. It is also shown that hipparaffin differs most markedly in melting point and solubility in alcohol both from ethylidene- and ethylene-dibenzamide. Further, ethylidene-dibenzamide decomposes at  $130^\circ$  in presence of water into aldehyde and benzamide, and ethylene-benzamide, on addition of soda, yields ethylenediamine and benzoic acid, but hipparaffin is unaltered. Again, when ethylidene-dibenzamide is boiled with sulphuric acid, it yields ammonia, benzoic acid, and ethaldehyde, whilst hipparaffin under the same conditions yields methaldehyde. This latter reaction would tend to show that hipparaffin is probably methylene dibenzamide; and to prove this conjecture, this compound was prepared synthetically from benzonitrile and methylal. The resultant substance was found to be identical in chemical and physical properties with hipparaffin, whose formation from hippuric acid can be represented by the equation  $2CH_2(NH\bar{B}z).COOH + 4O = CH_2(NH\bar{B}z)_2 + 3CO_2 + 2H_2O$ .

V. H. V.

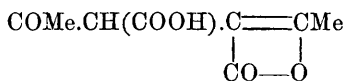
**Benzoylactic Acid.** II. By A. BAEYER and W. H. PERKIN, Jun. (*Ber.*, **17**, 59—66).—By the action of iodine on ethyl sodacetate, Harrow (*Annalen*, **201**, 145) obtained ethyl diacetosuccinate; by boiling with dilute sulphuric acid, this is decomposed into alcohol and ethyl carbopyrotritarate, the latter becoming saponified by continued boiling. Ethyl benzoylacetate exhibits a perfectly similar behaviour: ethyl dibenzoylsuccinate,  $C_{22}H_{22}O_6$ , crystallises in small colourless prisms melting at  $125$ — $126^\circ$ ; when warmed with concentrated sulphuric acid, it becomes first olive-green and then brownish-red; it dissolves in alcoholic potash with a yellow coloration. The lactonic acid,  $C_{18}H_{12}O_5$ , obtained on boiling it with 30 per cent. sulphuric acid, is sparingly soluble in water, readily in alcohol, ether, and benzene, and crystallises in small needles melting at  $230^\circ$  with decomposition. From the similarity between this reaction and that described by Harrow (*loc. cit.*), this acid may be assumed to be carbopyrotritaric acid, in which two phenyl-groups replace methyl. According to Harrow, carbopyrotritaric acid is a monobasic lactonic acid, and is converted into a dibasic acid by boiling with alkalis. The

authors, however, have as yet obtained only dibasic salts of their acid, showing that the aromatic compound takes up the elements of water with greater readiness; the calcium salt,  $C_{18}H_{12}O_6Ca$ , and the silver salt,  $C_{18}H_{12}O_6Ag_2$ , form white amorphous precipitates. When the monolactone is boiled with acetic anhydride and the product poured into water, the *dilactone* of dibenzoylsuccinic acid,  $C_{18}H_{10}O_4$ , separates in colourless scales of silvery lustre. It melts at  $254-255^\circ$  with decomposition, dissolves sparingly in hot alcohol with a splendid violet fluorescence. It is not attacked by alkaline carbonates, but alcoholic potash reconverts it into the original substance.

From the greater instability of the  $\beta$ -lactones, it is probable that the above compounds contain  $\gamma$ -lactone-rings, in which case they stand in a simple relationship to pulvic acid and anhydride:—



The monolactone of dibenzoylsuccinic acid, when heated, behaves differently from carbopyrotritaric acid, this yielding carbonic anhydride and pyrotritaric acid; whilst the former yields a sublimate (probably the diketone) insoluble in ammonia. This difference may perhaps be accounted for on the supposition that carbopyrotritaric acid contains a  $\beta$ -lactone-ring:—



When ethyl benzoylacetate is boiled, it is decomposed with formation of dehydrobenzoylactic acid,  $C_{18}H_{12}O_4$ , the reaction corresponding with the similar production of dehydracetic acid from ethyl acetoacetate:— $2C_6H_5.CO.CH_2.COOEt = C_{18}H_{12}O_4 + 2C_2H_5O$ . It crystallises from alcohol in long yellow needles melting at  $171-172^\circ$ , and is also readily soluble in ether and chloroform. With cold concentrated sulphuric acid, it forms an olive-green solution, which becomes violet on warming, and then exhibits the absorption-bands of indigo, the colour disappearing, however, on dilution with water. The alkali salts are readily soluble, whilst the silver salt,  $C_{18}H_{11}O_4Ag$ , forms a white flocculent precipitate unacted on by light. A solution of the ammonium salt yields a blackish-violet amorphous precipitate with ferrous sulphate, and a deep scarlet-red precipitate with ferric chloride. By the action of sodium amalgam, two crystalline acids are produced,  $C_{18}H_{14}O_3$  melting at  $112^\circ$ , and  $C_{18}H_{14}O$  melting at about  $145-150^\circ$  with decomposition. By the action of cold concentrated alcoholic potash on dehydrobenzoylactic acid, benzoylactic acid is reproduced in almost theoretical amount.

A. K. M.

**Action of Phosphorus Pentachloride on Amido-comenic Acid.** By T. BELLMANN (*J. pr. Chem.* [2], 29, 1—22).—How observed that when comenic acid was boiled with ammonia, it yielded a nitrogen-derivative, which he considered to be an amido-acid, and which he consequently called amido-comenic acid. Later researches have shown it to be a monobasic oxy-acid containing nitrogen in the radical nucleus. Ost found that when acted on by phosphorus pentachloride, all the oxygen and nitrogen were replaced by chlorine, hydrochloric acid was liberated, and hexachloropicoline,  $C_6HCl_6N$ , was formed. The author has studied the action of phosphorus pentachloride at various temperatures and in various proportions, carefully examining the bye-products formed.

I. *Action of 5 mols.  $PCl_5$  on 1 mol. Amido-comenic Acid at 220—250° and at 275°.*—After heating, the mass is thrown into iced water, whereupon a dark-coloured oil separates out. It constitutes the principal product of the reaction, and consists of a mixture of penta- and hexa-chloropicoline. The aqueous portion is evaporated until it crystallises. The crystals, which consist of a chlorinated substance, are separated from the liquor, dissolved in hot water and neutralised with ammonia, in order to separate the body from admixed compounds by the difference in solubility of its ammonium salts. On decomposing it with calcium chloride, the calcium salt is obtained in fine white silky needles. The free acid, which the author calls *monochloro- $\gamma$ -hydroxypicolinic acid*,  $C_6H_4ClNO_2 + H_2O$ , forms small colourless pointed needles, which are almost insoluble in cold water, but more soluble in hot. Its aqueous solution, which has an acid reaction, gives a slightly yellow coloration with ferric chloride. It yields a white precipitate with silver nitrate. The free acid melts at 224°. It forms a hydrochloride, crystallising in fine pointed needles.

The *normal calcium salt* forms white efflorescent needles. It is prepared by adding calcium chloride to a solution containing an insufficient quantity of ammonia to neutralise it. The *basic calcium salt* is obtained as a yellowish-white crystalline powder on adding calcium chloride to a neutral solution. Monochloro- $\gamma$ -hydroxypicolinic acid, when treated with tin and hydrochloric acid, is reduced to  $\gamma$ -hydroxypicolinic acid,  $C_6H_5N(OH).COOH + H_2O$ , which crystallises in small transparent rhombic pinakoidal plates, containing 1 mol.  $H_2O$ , melting at 258°: it differs widely in crystalline form from the  $\alpha$ - and  $\beta$ -acids. The *normal barium salt*,  $(C_6H_4NOH.COO)_2Ba$ , forms slightly yellow microscopic prisms. The *normal calcium salt* crystallises in groups of small white needles, containing 4 mols.  $H_2O$ . They become slightly red on standing in the air.

When the aqueous mother-liquor, which remains after separating the monochloro- $\gamma$ -picolinic acid, is neutralised with concentrated ammonia, it yields a mass of crystals from which the ammonium salt of a new acid can be separated, as it is less soluble than the crystals of ammonium phosphate and chloride. This salt yields a blue coloration with ferric chloride. The author proposes to call it temporarily *monochlorocyamic acid*. It crystallises with 1 mol.  $H_2O$  in white silky plates, melting at 186°, and resembling comenic acid. Its *silver salt*,  $C_7H_4ClNO_2.COOAg$ , forms a voluminous precipitate, which, on

stirring, becomes powdery. It is decomposed by boiling with water. The *barium salt* forms small white prisms, which become slightly red on exposure to the air.

II. *Action of 3 mols. of  $PCl_5$  on 1 mol. of Comenic Acid at  $200^\circ$ .*—The principal product is an oil consisting of a mixture of picoline penta- and hexa-chlorides. Mixed with it, in proportions varying directly with the temperature, are small quantities of monochloro- and  $\gamma$ -hydroxy-picolinic acid and chlorocyamic acid.

III. *Action of 3 mols.  $PCl_5$  on 1 mol. at Boiling Point.*—As soon as the reaction has moderated, the contents of the retort are heated until no more hydrochloric acid is evolved. The phosphorus oxychloride is then distilled off as far as possible, and the residue in small portions is thrown into ice-cold water. The amorphous body which separates out is probably a chloride with the composition  $C_5H_3Cl_3N.COCl$ , combined with phosphoric acid. On reduction, it yields the compound  $C_5H_7NO_2$ . Ost considers the latter to be the aldehyde of a dihydrohydroxypyridine-carboxylic acid,  $C_5H_5N(OH).COH$ . However, as it is not altered by sodium amalgam, it cannot be an aldehyde, but is more probably *methylhydroxypyridone*,  $C_5H_3NO(OH).CH_3$ . It crystallises in large transparent rhombic prisms, with well-formed basic pinakoids. It forms a crystalline acetyl-compound. The *phosphoric acid compound* crystallises in small white warty masses, containing no water of crystallisation; they become reddish on standing in the air. The *hydrochloride* forms long pointed needles, which are very soluble in cold water. A *sodium compound* could not be obtained. The author failed to convert the compound into the corresponding acid. Potassium permanganate converts it into oxalic acid. When treated with bromine, bromomethylhydroxypyridone is obtained, crystallising in small glittering anhydrous plates resembling amido-comenic acid.

*Action of Hydriodic Acid on Methylhydroxypyridone.*—An excess of hot fuming hydriodic acid was heated with methylhydroxypyridone in a sealed tube at  $275^\circ$ . Ammonium iodide was found in the solution. After separating the precipitated iodine, the mother-liquor was distilled with caustic soda into hydrochloric acid. Platinum chloride was then added, and the ammonium platinochloride removed by filtration. The filtrate yielded crystals of a new platinochloride, which, when decomposed with caustic soda, gave the characteristic smell of a pyridine base.

*Action of Phosphorus Pentachloride on Methylhydroxypyridone.*—When methylhydroxypyridone is heated with phosphorus pentachloride at  $200^\circ$  in the ratio of 1 to 5—adding phosphorus oxychloride—hexachloropicoline, melting at  $60^\circ$ , and monochloro- $\gamma$ -hydroxypicolinic acid, melting at  $224^\circ$ , are formed. J. I. W.

**Vulpic Acid.** By A. SPIEGEL (*Annalen*, **219**, 1—56).—In this paper, a detailed account is given of the direct derivatives, the products of the reduction and of oxidation of pulvic acid, and of oxytolylic acid, and of the constitutional formulæ of pulvic and vulpic acids (Abstrs., 1881, 97, 173, 1036; 1882, 1076). A. B.

**Naphthalene Derivatives.** By I. GUARESCHI (*Annalen*, **222**, 262—300).—Besides the dibromonaphthalene melting at  $81^{\circ}$ , described by Glaser, and that melting at  $61^{\circ}$  of Jolin, the author has obtained isomerides melting at  $67.5$ — $68^{\circ}$  and  $130$ — $131.5^{\circ}$ . *Dibromonaphthalene* melting at  $81$ — $82^{\circ}$  boils with slight decomposition at  $310^{\circ}$ ; at  $56^{\circ}$ , 1 part dissolves in 16.5 parts alcohol. On oxidation with nitric acid, it yields dibromophthalic acid, monobromomononitrophthalic acid, and a mixture of dibromonitronaphthalenes; and with chromic acid in acetic acid solution, dibromonaphthaquinone and dibromophthalide. From these reactions, the author considers the constitutional formula of this dibromo-compound to be  $[\text{Br} : \text{Br} = 1 : 4]$ .

*Dibromonaphthalene*, melting at  $130$ — $131.5^{\circ}$ , boils also with some decomposition at  $325.5^{\circ}$ ; at  $56^{\circ}$ , 1 part dissolves in 50 parts alcohol. No dibromonaphthaquinone could be obtained from this isomeride. With nitric acid, it yields a monobromonitrophthalic acid and other products. Jolin obtained this dibromo-compound by acting on  $\alpha$ -dinitronaphthalene with phosphorus pentabromide, and as this  $\alpha$ -derivative contains a nitro-group in each ring, probably this dibromonaphthalene has a similar constitutional formula. *Dibromonaphthalene tetrabromide* can be obtained from the first-mentioned dibromo-compound (m. p.  $81$ — $82^{\circ}$ ), but could not be obtained from that melting at  $130$ — $131.5^{\circ}$ . *Dibromophthalic acid*,  $\text{C}_6\text{H}_2\text{Br}_2(\text{COOH})_2$ , obtained as mentioned above, is a white crystalline powder, soluble in hot water and in alcohol, and melting at about  $135^{\circ}$ . The sodium salt is precipitated by a mixture of alcohol and ether in bright anhydrous laminae, and is very soluble in water. The anhydride,  $\text{C}_6\text{H}_2\text{Br}_2(\text{CO})_2\text{O}$ , obtained by heating the acid, melts at  $207.5$ — $208^{\circ}$ , and sublimes in beautiful iridescent needles; when slowly heated with sulphuric acid and benzene, it gives a violet-purple colour.

*Dibromonaphthaquinone*,  $\text{C}_{10}\text{H}_4\text{Br}_2\text{O}_2$ , is insoluble in water; at  $16^{\circ}$ , 1 part dissolves in 290—300 parts alcohol. It crystallises in gold-yellow needles melting at  $171$ — $173^{\circ}$ , and distils in steam. It is isomeric with that (melting at  $149.5^{\circ}$ ) obtained by Diehl and Merz (*Ber.*, **11**, 1064). Dibromophthalide,  $\text{C}_8\text{H}_4\text{Br}_2\text{O}_2$ , crystallises from hot alcohol in white prismatic needles melting at  $188$ — $189^{\circ}$ .

By the action of bromine on nitronaphthalene melting at  $59^{\circ}$ , the author obtained monobromonitronaphthalene, dibromonaphthalene, and two tetrabromides of nitronaphthalene, which are always formed even when little bromine is used. *Dibromonitronaphthalene*,  $\text{C}_{10}\text{H}_5\text{Br}_2\text{NO}_2$ , is formed in small quantities, and crystallises from alcohol in small yellow needles melting at  $96.5$ — $98^{\circ}$ .  $\alpha$ -*Nitronaphthalene tetrabromide*,  $\text{C}_{10}\text{H}_7\text{NO}_2\text{Br}_4$ , is sparingly soluble in alcohol (at  $15^{\circ}$ , 0.26 part dissolves in 100 parts alcohol), and crystallises in groups of colourless needles melting at  $131^{\circ}$ ; when heated to  $135$ — $137^{\circ}$ , it gives off bromine and hydrobromic acid, and yields bromonitronaphthalene and in part the  $\beta$ -isomeride melting at  $142$ — $143.5^{\circ}$ . By prolonged boiling with alcohol, it yields a  $\gamma$ -isomeride melting at  $172$ — $173^{\circ}$ ; this is also formed along with the  $\alpha$ -derivative in the original reaction. At the melting point, the  $\gamma$ -isomeride decomposes with evolution of bromine and hydrobromic acid, and formation of bromonitronaphthalene,  $\text{C}_{10}\text{H}_7\text{NO}_2\text{Br}_4 = \text{C}_{10}\text{H}_5\text{BrNO}_2 + \text{HBr} + \text{Br}_2$ . *Bromonitro-*

*naphthalene*,  $C_{10}H_6Br.NO_2$ , obtained by the direct action of bromine on nitronaphthalene, and by the decomposition of nitronaphthalene tetrabromide, crystallises from alcohol in yellow needles which melt at  $122.5^\circ$ , and are soluble in ether, benzene, acetic acid, and chloroform. In cold alcohol, 1 part is soluble in 297 parts. By oxidation with potassium permanganate, it is converted into monobromophthalic acid,  $C_6H_3Br(COOH)_2$ , which crystallises in small white prismatic needles melting at  $174-176^\circ$ ; it is soluble in water, alcohol, and ether, but insoluble in chloroform, and yields an anhydride. The barium, lead, and silver salts are nearly insoluble. The anhydride crystallises in colourless needles which melt at  $132^\circ$ ; with sulphuric acid and benzene, it yields a purple-violet colouring matter, probably a bromophthalein. This monobromophthalic acid is probably isomeric with that obtained by Faust (m. p.  $138-140^\circ$ ), by the direct action of bromine on phthalic acid (*Annalen*, **160**, 62), and identical with Smith's (*Jahresb.*, 1879, 143) melting at  $125^\circ$ , as the author has observed that even traces of impurity will lower the melting point  $5^\circ$  or  $6^\circ$ .

Nitrobromonaphthalene, melting at  $122.5^\circ$ , on reduction, yields *amidobromonaphthalene* melting and subliming at  $63-64^\circ$ . It crystallises in fine plates, sparingly soluble in boiling water, easily in alcohol, ether, benzene, and chloroform; it becomes red on exposure to light, and behaves towards ferric chloride, silver nitrate, &c., as an amidonaphthalene. The hydrochloride crystallises in plates, sparingly soluble in cold water, and still less in hydrochloric acid solution. By oxidation with potassium permanganate, it yields the above-described bromophthalic acid. An isomeric amidobromonaphthalene was also prepared from Jolin's mononitrobromonaphthalene melting at  $85^\circ$  as an oil soluble in alcohol and ether, but not crystallising therefrom.

A. B.

**Resin Essences and Oils.** By A. RENARD (*Ann. Chim. Phys.* [6], **1**, 223—255).—The products of the fractional distillation of resin or colophony are separated into two classes, viz., the more volatile portions collectively known by the commercial name of the essences, and the oils whose boiling points are near  $300^\circ$ . By the distillation of large quantities of resin, the author has separated the former class into the following constituents:—

#### *Hydrocarbons.*

	B. p.
Pentane, $C_5H_{12}$ .....	35—38°
Amylene, $C_5H_{10}$ .....	35—40
Hexane, $C_6H_{14}$ .....	64—66
Hexylene, $C_6H_{12}$ .....	67—70
Toluene hexahydride, $C_7H_{14}$ .....	95—98
Toluene tetrahydride, $C_7H_{12}$ .....	103—105
Toluene, $C_7H_8$ .....	111
Xylene hexahydride, $C_8H_{16}$ .....	120—123°
Xylene tetrahydride, $C_8H_{14}$ .....	128—130
Xylene, $C_8H_{10}$ .....	136

*Hydrocarbons.*

	B. p.
Cumene hexahydride, $C_9H_{18}$ .....	147—150
Cumene tetrahydride, $C_9H_{16}$ .....	155 ?
Cumene, $C_9H_{12}$ .....	151
(1) Terebenthene, $C_{10}H_{16}$ .....	154—157
(2) Terebenthene, $C_{10}H_{16}$ .....	171—173
Cymene hexahydride, $C_{10}H_{20}$ .....	171—173
Cymene, $C_{10}H_{14}$ .....	175—178
Metapropyl-ethylbenzene, $C_{11}H_{16}$ ..	193—195
Diocetene, $C_{16}H_{28}$ .....	260

*Aldehydes.*

Isobutaldehyde .....	60—62
Valeraldehyde .....	96—98

*Acids.*

Isobutyric acid .....	153—155
Valeric acid .....	173—175

Of these compounds the hexa- and tetra-hydrides of toluene, xylene, cumene, and cymene only need be specially noticed. The former or hexahydrides are probably identical with the hydrocarbons obtained by Beilstein and Kurbatow, and by Schützenberger, from the Caucasian petroleum; they are polymeric with the olefine series. *Toluene hexahydride*,  $C_7H_{14}$ , boils at 95—98°, sp. gr. = 0.742; it is soluble in alcohol and ether, and is not acted on by hydrochloric acid; with nitric and sulphuric acids, it does not furnish nitro- or sulphonic acid derivatives; by concentrated nitric acid, it is converted into oxalic acid. Cumene hexahydride boiling at 147—150°, and cymene hexahydride boiling at 171—173°, are identical in chemical properties with the above hydrocarbon.

*Toluene tetrahydride*,  $C_7H_{12}$ , boils at 103—105°, sp. gr. = 0.737; it rapidly absorbs oxygen, and is soluble in alcohol and ether. By the action of bromine under various conditions it is converted into two hexabromo-,  $C_7H_6Br_6$ , and one dibromo-derivative,  $C_7H_{10}Br_2$ . The first forms crystals which melt at 134°, and at a rather higher temperature decompose with evolution of hydrobromic acid: its isomeride decomposes at about 150°; the dibromide forms white, very unstable crystals. On leaving toluene tetrahydride in contact with water for some time, there are formed long white crystals of a dihydrate,  $C_7H_{12} \cdot 2H_2O$ , identical with the colophene hydrate obtained by Tichborne and Anderson. On treatment with sulphuric acid, two isomeric polymerides of the formula  $C_{14}H_{24}$  are formed, the one a pale yellow oil, readily oxidised, and the other, a colourless oil, unaltered by the air. *Xylene tetrahydride*,  $C_8H_{14}$ , boils at 129—132°, sp. gr. = 0.8158, forms a tribromo- and dibromo-derivative, of which the former,  $C_8H_{11}Br_3$ , is an orange colour, the latter, a colourless oil; they are both readily decomposed with evolution of hydrobromic acid. By



sulphuric acid, the hydrocarbon yields a polymeride,  $C_{16}H_{28}$ , a yellow oil, readily oxidised in contact with air. Cumene tetrahydride was obtained only in small quantities.

In their chemical properties, the terpenes resembled ordinary terebenthene, they are both lævorotatory. The observations of Kelbe (Abstr., 1882, 711) on the cymene and isobutyric and valeric aldehydes and acids, are confirmed in detail.

The resin oils seem to consist principally of more or less readily oxidised hydrocarbons, probably polymeric with the known hydrocarbons of generic formula,  $C_nH_{2n-2}$ . On treatment with sulphuric acid, they are separated into two distinct portions, one insoluble in the acid, not readily oxidised by air; the other soluble in the acid, and readily converted into resins by absorption of oxygen.

V. H. V.

**A Glucoside from Boldoa Fragrans.** By P. CHAPOTEAUT (*Compt. rend.*, **98**, 1052—1053).—The leaves of *Boldoa fragrans* are treated with boiling alcohol, the solution evaporated to dryness, and the residue extracted with very dilute hydrochloric acid in order to remove the alkaloïd described by Bourgoïn and Verne. The liquid, freed from the greater part of the mucilaginous matter, is then treated with ether or chloroform, and this ethereal or chloroform solution, on evaporation, leaves a transparent amber-coloured syrup with an aromatic taste and smell. This substance, which exists in the leaves to the extent of 0.3 per cent., has the composition  $C_{30}H_{52}O_8$ , and can be distilled in a current of steam, but cannot be distilled without decomposition in a vacuum or in a current of hydrogen. When heated with very dilute hydrochloric acid, it yields glucose, methyl chloride, and a syrupy substance of the composition  $C_{19}H_{26}O_3$ , which dissolves in alcohol and benzene, but is insoluble in water. If the benzene solution is treated with sodium, hydrogen is evolved; and if the sodium-derivative thus formed is treated with alcoholic iodides, methyl- or ethyl-derivatives can be obtained. The substance,  $C_{30}H_{52}O_8$ , is therefore a glucoside or, rather, an ether in which glucose plays the part of an acid. The constitution of the alcoholic constituent has not yet been ascertained.

When the glucoside is injected under the skin of a guinea-pig, or taken into the stomach of a dog, it produces a quiet sleep of longer or shorter duration. If injected into the blood of the dog, it excites and increases the secretory functions, especially the secretion and excretion of bile, saliva, and urine.

C. H. B.

**Picrotoxin.** By E. SCHMIDT (*Annalen*, **222**, 313—352).—The greater part of this paper has already appeared (Abstr., 1881, 740). The author still considers that picrotoxin is a chemical compound of picrotoxinin and picrotin, contrary to the opinion of Barth and Kretschy (Abstr., 1881, 286) that it is a mixture of these two substances. He gives as the formula for picrotoxin,  $C_{30}H_{34}O_{13}$ ; for picrotoxinin,  $C_{15}H_{16}O_6 + H_2O$ ; and for picrotin,  $C_{15}H_{18}O_7$ . By the action of benzoic chloride on picrotoxinin he obtained picrotoxinin-benzoic anhydride,  $(C_{15}H_{16}O_6)_2, \overline{Bz}_2O$ , melting at 237—238°, nearly

insoluble in water, but soluble in hot alcohol, and crystallising in colourless needles. By acting in a similar way on picrotin, he obtained benzopicrotin,  $C_{15}H_{15}O_6, \overline{Bz}O$ , melting at  $245^\circ$ , and crystallising from alcohol in colourless needles. A. B.

**Picrotoxin.** By L. BARTH and M. KRETSCHY (*Monatsh. Chem.*, **5**, 65—71).—A criticism of the work of Schmidt on picrotoxin (preceding Abstract). The authors adhere to their view that picrotoxin is a mixture of picrotoxinin and picrotoxin or picrotin, and that the formula of the latter substance is  $C_{25}H_{30}O_{12}$ . A. J. G.

**Morin.** By R. BENEDIKT and K. HAZURA (*Monatsh. Chem.*, **5**, 63—64).—By treating morin, suspended in glacial acetic acid, with nitric acid, there are obtained oxalic acid, some amorphous products, a small quantity of a nitro-derivative, and resorcylic acid. The amount of the last acid was 18 per cent. of the morin employed. According to Hlasiwetz and Pfaundler (*J. pr. Chem.*, **94**, 65), morin is readily reduced by sodium-amalgam, yielding phloroglucinol only: as it is very unlikely that that portion of the morin molecule which yields resorcylic acid on oxidation would yield phloroglucinol on reduction, it seems probable that some other reduction product has been overlooked. A. J. G.

**Quercetin and its Derivatives.** By J. HERZIG (*Monatsh. Chem.*, **5**, 72—93).—The constitution of quercetin is still uncertain. Hlasiwetz and Pfaundler (*J. pr. Chem.*, **94**, 65) have shown that on fusing it with potash, phloroglucinol and protocathechuic acid are obtained as end-products, and what is much more important, that by reduction with sodium-amalgam, phloroglucinol and protocathechuic alcohol are formed. Liebermann and Hamburger have shown quercetin to have the formula  $C_{24}H_{16}O_{11}$ , and have described a diacetyl and a disodium derivative from which they draw the conclusion that only two hydroxyl groups are present (*Abstr.*, 1879, 944). Quercetin crystallises with 3 mols. of water. When heated at  $140$ — $150^\circ$  with concentrated hydrochloric acid, it does not yield methyl or ethyl chloride; heated with hydrochloric acid and alcohol, it does not yield an ethyl salt.

*Hexethylquercetin*,  $C_{24}H_{10}Et_6O_{11}$ , is prepared by dissolving 1 molecular proportion of quercetin in 4—5 of alcoholic potash, and then heating with the corresponding amount of ethyl iodide in a sealed tube at  $100^\circ$  for 12 hours. It crystallises in long yellow needles, melts at  $120$ — $122^\circ$  (uncorr.), and is sparingly soluble in cold alcohol. The yield only corresponded to about 50—55 per cent. of the quercetin employed. With potash, it forms a very unstable compound insoluble in alcohol, decomposed on washing with alcohol or water. On heating hexethylquercetin (1 part) with alcoholic potash (5—6 parts) in sealed tubes at  $140$ — $150^\circ$ , a very complete decomposition is effected, the main product of the reaction (53—57 per cent.) being diethylprotocatechuic acid, the identity of which with Kölle's acid (this Journal, 1871, 830) was proved by a comparison of the acid and its salts, and finally by the preparation of *ethylic diethylprotocatechuate* (m. p.  $56^\circ$ )

from both acids. The amount of diethyl protocathechuic acid obtained is nearly equal to that required on the assumption that 1 mol. hexethylquercetin yields 2 mols. of the acid.

*Hexamethylquercetin*,  $C_{24}H_{10}Me_6O_{11}$ , prepared in a manner similar to the ethyl salt, crystallises in long golden needles, melts at  $156-157^\circ$  (uncorr.), and when heated with excess of alcoholic potash yields dimethylprotocatechuic acid. On heating hexamethylquercetin with 8-10 parts of acetic anhydride and sodium acetate for 3-4 hours, *diacetylhexamethylquercetin*,  $C_{24}H_8Me_6Ac_2O_{11}$ , is obtained, crystallising in silvery-white needles, melting at  $167-169$ , and sparingly soluble in cold absolute alcohol. On saponification with baryta, it again yields hexamethylquercetin.

The author endeavoured to prepare the diacetylquercetin (m. p.  $196-198^\circ$ ) described by Liebermann and Hamburger (*loc. cit.*), but found the product to be *octacetylquercetin*,  $C_{24}H_8Ac_8O_{11}$ ; this melts at  $189-191^\circ$ , but otherwise exhibits properties identical with those of the substance they described.

The author considers that these results show quercetin to contain at least six hydroxyl-groups, and also that two protocathechuic acid residues must exist preformed in it.

A. J. G.

**Contributions to the Histochemistry of Plants.** By A. ROSSOL (*Monatsh. Chem.*, 5, 94-107).—I. *Helichrysin* is a yellow pigment contained in the involucre bracts of *Helichrysum bracteatum*, *H. arenarium*, *H. foetidum*, *H. hebelepsis*, and *Statice Bonduelli*. In the young bracts, it occurs in the homogeneous protoplasmic cell contents, whilst in the old bracts it is found in the cell membranes only. To obtain it, the flowers are extracted with strong alcohol, the solution evaporated to dryness, the residue treated with water, and the aqueous solution evaporated to dryness at a low temperature. The residue was extracted with absolute alcohol, the solution, after dilution with water, precipitated with lead acetate, the red precipitate well washed, suspended in water and decomposed by hydrogen sulphide; the filtrate on evaporation at  $40-50^\circ$  yields helichrysin as an amorphous, lustrous dark-yellow mass. It is sparingly soluble in cold, readily soluble in boiling water, in alcohol, ether, and acetic, oxalic and tartaric acids, insoluble in benzene, chloroform, and carbon bisulphide. The alcoholic solution has a neutral reaction, and is of a fine golden-yellow colour; addition of either mineral acids or alkalis changes the colour to purple-red, the yellow tint being restored on neutralisation. In alkaline solution, it is readily reduced by sodium amalgam or sulphurous acid.

II. The orange-red colouring matter of the fungi *Peziza aurantia* and *P. convexula* occurs in union with an oily substance dissolved in the plasma of the paraphyses. It dissolves readily in alcohol and ether, sparingly in benzene; the colour is not altered by alkalis or organic acids, is changed to light green by nitric acid, and is destroyed by hydrochloric acid.

III. Using the colour test with sulphuric acid as a means of detecting the position of saponin in the microscopic examination of sections of the roots of *Saponaria officinalis* and *Gypsophila struthium*, the

author finds that it occurs dissolved in the contents of all the cells of the parenchyma of the cuticular layer, of the medullary rays and of the wood parenchym and in the parenchyma cells of the cuticular layer of the roots of *Quillaia saponaria*. On drying the plants, it separates in minute amorphous masses.

IV. In the fruits of *Strychnos nux vomica* and *S. potatorum*, strychnine is found to occur in solution in the oil drops suspended in the cells of the endosperm. A. J. G.

**Chlorophyll; a Compound of Iron with Glucoside.** By A. B. GRIFFITHS (*Chem. News*, 49, 237).—Arguing from the results published on the probability of chlorophyll being a glucoside (Schunck, *Proc. Roy. Soc.*, 36, 183), and from the presence of ferrous sulphate in plant cells (Abstr., 1883, 195), and also from the production of a blue colour when Schunck's chlorophyll (*loc. cit.*) is mixed with potassium ferricyanide, it is suggested that the function of ferrous sulphate in the plant is to supply iron to the colourless glucosides (leukoplastids), and so convert them into green glucosides (chlorophyll), whilst the sulphur acts as food to the protoplasm; this would make chlorophyll a compound of iron with a glucoside. It is shown that green chlorophyll is never found in plants grown on soils free from iron: moreover, the author has grown plants to maturity in solutions containing all inorganic salts necessary for plant life, all the sulphur in solution being as ferrous sulphate. D. A. L.

**Bark of "Bois Piquant."** By E. HECKEL and F. SCHLAGDENHAUFFEN (*Compt. rend.*, 98, 996—998).—The bark examined was the variety peculiar to Guiana, and agreed exactly with Guibout's description of *Zanthoxylum caribæum*. Its anatomical structure is entirely different from that of angustura bark, which it resembles in external appearance. When macerated with water, it yields a bitter, slightly acid, yellow solution, which turns brown with ferric chloride, and yields an abundant yellow precipitate with mercuric chloride, stannous chloride, tannin, picric acid, double iodides, or phosphomolybdic acid, but gives only a slight turbidity with lead acetate. Nitric acid produces a deep red colour. When extracted with light petroleum, the bark yields a considerable quantity of chlorophyll, fat, and wax, together with a crystalline substance which can also be extracted by alcohol. This substance forms colourless needles of the composition  $C_{12}H_{24}O$ , which melt at  $285^{\circ}$ , and give no coloration with nitric, sulphuric, or hydrochloric acid.

If the alcoholic extract, after separation of these crystals, is diluted with water, mixed with lime, evaporated to dryness, and the residue extracted with boiling alcohol, a second crystalline substance is obtained which resembles the vegetable alkaloids in its general properties. It exists in the bark only in very small quantities. With nitric acid, it gives a deep-red coloration, but if the liquid is evaporated on a water-bath and mixed with stannous chloride, no violet colour is produced. Sulphuric and hydrochloric acid have no action on it, but sulphuric acid and potassium dichromate, manganese dioxide, or lead dioxide, produce a violet coloration similar to that produced by strychn-

nine mixed with a little selenium. An alcoholic solution of bromine also produces a deep blue coloration which persists for a long time. 5 mgrms. of this alkaloid injected in aqueous solution beneath the skin of a frog, produce rapid general paralysis, followed by death in about half an hour, and similar effects are observed with rabbits and guinea-pigs.

A nitrogenous resinous substance, soluble in water, was also obtained from the bark. It has the general properties of the alkaloids, and in its physiological action very closely resembles the crystalline alkaloid just described, although it differs from it in physical properties. None of the so-called xanthopicrite could be obtained from the bark.

C. H. B.

**Decomposition Products of Albumin.** By W. KÜHNE and R. H. CHITTENDEN (*Zeits. f. Biol.*, 19, 159—208).—Kühne from his former researches regards the albumin molecule as composed of two groups (antialbumid and hemialbumin) preformed in it, which are converted into their corresponding peptones by the action of pepsin. Antialbumose and hemialbumose are the intermediate bodies between albumin and peptone, both being produced by the action of pepsin, as well as by weak acid. The two peptones are distinguished by their behaviour under the influence of trypsin. Hemi-peptone is converted into leucine and tyrosine, only a small quantity of peptone remaining unchanged, whilst anti-peptone on the other hand is unaltered even after long-continued digestion. The authors give an exact description of the behaviour and general properties of these different bodies obtained from egg-albumin, serum-albumin, syntonin, and fibrin. The following table gives the mean of many analyses of the chief bodies:—

	Antialbumid.	Antipeptone.	Hemialbumose.	Hemi-peptone.
C .....	53.79	49.87	50.96	49.38
H .....	7.08	6.89	6.85	6.81
N .....	14.55	15.21	15.88	15.07
S .....	} 24.58	28.03	{ 1.45	1.10
O .....			{ 24.86	27.64

Antialbumid is best obtained from coagulated egg-albumin by heating for a long time in 0.5 per cent.  $\text{H}_2\text{SO}_4$ , washing the undissolved residue with water, digesting with pepsin, which however does not dissolve it, but converts it into a substance of jelly-like consistency, finally digesting with trypsin in an alkaline medium. Antipeptone may be obtained from the solution by precipitation with alcohol. No leucine or tyrosine was formed by long digestion of the antipeptone. Antialbumose can only be obtained by a process of fractional peptic digestion, and when digested tryptically, forms antipeptone only.

Hemialbumose and hemi-peptone are best obtained by acting on coagulated egg-albumin for a short time with a peptic fluid. The solution thus obtained is neutralised, the precipitate filtered off, the filtrate evaporated down to a small bulk and precipitated with alcohol. The hemialbumose and hemi-peptone are separated by extracting the peptone with cold water.

The authors give full details for preparing these bodies from serum-albumin and fibrin. Digesting fibrin tryptically for a short time is another good way of obtaining antialbumid. Hrmialbumose like hemipeptone on digestion furnishes leucin and tyrosin.

J. P. L.

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## Physiological Chemistry.

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**Influence of Potassium Bromide on Nutrition.** By B. SCHULZE (*Zeits. f. Biol.*, 19, 301—312).—More or less accurate experiments have been made with the same view as the author's with morphine, quinine, digitalis, iodine, mercury, arsenic compounds, phosphorus, &c. Of the halogens, chlorine and iodine alone have been experimented with, the former as a sodium salt, the latter as hydriodic acid. Chloride of sodium produces a diuretic action, as well as an increase in the decomposition of albumin and a concomitant increase of nitrogen in the form of urea. Hydriodic acid on the other hand has no decided influence on the decomposition of albumin. The potash and soda salts have not been experimented with; the author presumes the action would be the same as that of the acid.

The favourable results that have been obtained by the use of bromide of potassium in different kinds of nervous disorders, especially epilepsy, lead one to the conclusion that the functions of the nervous system suffer a change under the influence of the drug. The author conducted the experiments on himself, taking a diet of known composition, and observing very regular habits. The drug was taken in 10-gram doses, divided into two portions of 5 grams each, dissolved in 200 c.c. water and taken at intervals of four hours. The daily ration was as follows:—

	Grams.
220 grams fresh meat, containing.....	7·13 N.
55 „ air-dried wheaten bread, containing	0·92 „
30 „ fat-free cocoa, containing .....	1·14 „
30 „ butter.....	—
30 „ sugar.....	—
5 „ salt.....	—
1500 c.c. water.....	—
Total .....	9·19 N.

The experiment lasted from the 4th to 13th July. On each day, the volume, sp. gr., and absolute weight of the urine were determined, as well as its nitrogen, sulphur, and phosphorus, a record also of the body-weight and temperature was kept (see table, p. 851). In the fæces, the nitrogen only was determined. The numbers obtained from the fæces were so irregular, that it was difficult to say whether the bromide had any influence on the digestion of the food.

Date.	Body-weight.	KBr, gram.	Volume, c.c.	Absolute weight.
July 4th .....	142·0	—	668·0	685·7
„ 5th .....	140·5	—	611·0	627·5
„ 6th .....	139·5	—	678·5	696·2
„ 7th .....	138·5	—	630·5	646·9
„ 8th .....	137·5	10	946·5	969·0
„ 9th .....	136·0	10	875·0	894·9
„ 10th .....	135·5	—	630·6	647·0
„ 11th .....	135·5	—	609·5	625·6
„ 12th .....	135·5	10	865·0	884·7
„ 13th .....	135·0	—	671·0	687·6

Date.	Specific gravity.	N.	S.	P.
July 4th .....	1·026	10·57	0·701	0·806
„ 5th .....	1·027	10·72	0·684	0·680
„ 6th .....	1·026	12·15	0·724	0·889
„ 7th .....	1·026	11·25	0·716	0·825
„ 8th .....	1·024	11·90	0·738	0·680
„ 9th .....	1·023	11·24	0·776	0·638
„ 10th .....	1·026	10·74	0·761	0·734
„ 11th .....	1·026	11·10	0·725	0·832
„ 12th .....	1·023	11·33	0·734	0·699
„ 13th .....	1·025	10·45	0·704	0·723

Taking the average of the first four days as the normal elimination, there is a large increase in the volume of urine on the day the drug was taken. On repeating the dose on July 9th, the increase was not so marked: this can only be explained, the author says, by the supposition that there was an insufficiency of water in the food and body to cause an increase in volume. The increased quantity of water eliminated is not connected with the excretion of the drug which passes in small quantities only on the first day, but in large quantities on the second day, when the amount of urine excreted is again normal.

When the nitrogen is taken alone, the influence of the bromide is not very clear, for on the 8th July there was a moderate increase; on the 9th, when a further increase might have been expected from the second dose, the nitrogen was normal. The sulphur and phosphorus, however, show a regular and marked change, the former an increase, the latter a decrease. The author supposes the balance of nitrogen elimination is attributable to the fact that the minus-nitrogen of the phosphorised constituents, nuclein, lecithin, and the plus-nitrogen from the increased decomposition of sulphur-yielding bodies, compensate each other. He concludes from this, that under the influence of bromide of potassium, a decided diminution of metabolism occurs in the nervous tissue, and along with it a decided diminution of nervous activity.

J. P. L.



**Cocoa-nut Meal for Horses.** (*Bied. Centr.*, 1884, 135.)—Some of the horses of the 7th Cuirassiers were fed with a mixture of oats and meal, and then compared with others fed only on oats: the results in the former case were most satisfactory, the reduction in the cost of the horse-keep amounting to 50 frs. per year. E. W. P.

**Rearing Calves on Skim Milk.** By A. BARTH and H. HENNINGSEN (*Bied. Centr.*, 1884, 120).—The first author says that feeding a calf from birth with skim milk, and calculating the value of the milk from the price obtained for the calf, raised the value of skim milk from 8 pfennigs per litre (market price) to 11.5 in the one case, and to 12.1 in the other. Henningsen on the other hand, with five calves fed on skim milk, after the eighth day reckons skim milk at 4 pfennigs. E. W. P.

**Formation of Neutral Fat from Fatty Acid in the Animal System.** By I. MUNK (*Bied. Centr.*, 1884, 106).—A dog was fed, after 19 days starving, for 14 days on 3200 grams flesh and 2850 grams of the acids obtained from mutton suet. At the end of that time, when the animal was killed, it was found that a large quantity of fat was deposited, and that it consisted of 96 per cent. of ordinary suet. Consequently, as the fat deposited had the composition of suet, it could not have been produced from the ordinary albuminoids given in the food, for that would have formed dog-fat. E. W. P.

**Properties of Linseed and Sesame Seed.** By LANGLEBERT (*Bied. Centr.*, 1884, 138).—By reason of the mucilage, these mucilaginous seeds have a double action. They act mechanically in the stomach by producing an increased flow of gastric juice, thus preventing debility of the stomach; softened in the stomach they pass into the intestines, and there the oil they contain forms an emulsion, and acts in its characteristic manner. E. W. P.

**Gases of the Alimentary Canal of Herbivora.** By TAPPEINER (*Zeits. f. Biol.*, 19, 228—279).—Previous observations have shown that a much larger quantity of gas is formed in the intestines of herbivora than of carnivora; at the same time, the aromatic products of the urine derived from putrefactive changes in the intestines are much greater. The author first endeavours to obtain a thorough survey of the gases formed in the different sections of the alimentary canal, and further to examine whether the bacteria can exert the same activity without as within the organism. In order to isolate the different sections, the abdominal cavity is opened immediately after death, and the various parts ligatured without disturbing the organs (*in situ*) more than possible. The collection of the gas in the case of the small animals was carried out under mercury. In the case of the larger animals, saturated salt solution was used in place of mercury, the transference of the gas being performed as quickly as possible.

As the composition of the gas developed in the intestines is modified by diffusion and solution in the blood, the author conducted after-fermentation experiments of the contents of the different sections, in

order to determine the true relation. These were performed in glass cylinders, kept at the most favourable temperature in an incubator. Bunsen's method of analysis was first used, afterwards that of Hempel. The author first examines the intestinal gases of the ruminants. The gas of the paunch was found to be of a very constant composition, consisting approximately of 65 per cent.  $\text{CO}_2$ , 31 per cent.  $\text{CH}_4$ , 2 to 4 per cent.  $\text{N}_2$ . The after-fermentation of the contents in the manner described, gave nearly the same results, the most characteristic features of the fermentation being the constant formation of  $\text{CH}_4$  and a large quantity of free acid. In the living animal, the contents of the paunch are maintained weakly alkaline or only faintly acid by the constant flow of saliva: directly the flow ceases, the reaction becomes acid. Oxygen in small quantities increases the activity, but in large quantities (as for instance exposing the contents for one hour to the air) retards fermentation. Magnesia also has a very marked influence on the fermentation, if added in a quantity of about 1 per cent.; at first only  $\text{CO}_2$  and  $\text{H}_2$  are given off, then  $\text{CO}_2$  and a little  $\text{CH}_4$ ; later on, the contents become acid, and the usual marsh-gas fermentation appears. If, however, the magnesia be added in a quantity of about 1.5 per cent., the fermentation is arrested for some weeks, and when the fermentation recommences,  $\text{CO}_2$  and  $\text{CH}_4$  are formed, but the contents throughout remain slightly alkaline, although from the development of the gas, relatively speaking, there must have been more than a sufficiency of acid to combine with the magnesia. The action of antiseptics is the same as in all other fermentative processes, total suspension, or hindrance according to the strength of the antiseptic.

The gases of the reticulum, manyplies, and rennet were not examined.

The production of gas in the small intestine appears to be less than in the paunch. The difference in composition is mainly due to diffusion undergone in transit. The after-fermentation of the contents of the small intestine yields almost exclusively  $\text{CO}_2$ ,  $\text{SH}_2$ , and  $\text{H}_2$ . The contents of the cæcum and colon similarly treated yield the same gases as the paunch contents, but less in quantity, and the reaction is feebly alkaline. From this it would appear as though there were two separate kinds of  $\text{CH}_4$  fermentations. The author advances two suppositions. 1st. If the acid and  $\text{CH}_4$  are developed by one and the same process, then there probably exists another species of bacterium in the colon capable of producing bodies of alkaline reaction which neutralise the acid. 2nd. If the two processes are distinct, the acid-producing bacterium is absent in the colon.

The author next examines the intestinal gases of the horse and rabbit.  $\text{CH}_4$  is not found as a constituent of the gas of the stomach, the gas being composed chiefly of  $\text{CO}_2$ ,  $\text{H}_2$ , and  $\text{N}_2$ . The small intestine gives the same results as the stomach. It is difficult to understand how the fermentation can proceed in presence of so much free hydrochloric acid in the stomach. The contents of the colon and cæcum subjected to after-fermentation become very acid,  $\text{CH}_4$  being produced; this is exactly the opposite result to that obtained in the case of ruminants.

The author then refers to the statement found in most text-books that the fermentative processes which go on in the paunch and colon

of herbivora result in the formation of lactic and butyric acids, and the development of  $\text{CO}_2$  and  $\text{H}_2$ , and claims that his experiments show that on an exclusively hay diet such is not the case, and goes on to describe experiments which in his opinion prove that these bodies are not produced even when beans and oats are substituted for half the hay.

In opposition to Hofmann, he finds that there is a development of  $\text{CH}_4$  in the large intestine of rabbits when fed on green food.

J. P. L.

**Hemialbumose in Urine.** By W. KÜHNE (*Zeits. f. Biol.*, **19**, 209—227).—The author examined the urine of a patient suffering from osteomalacia, which gave the reactions of Bence Jones's albumin, to which he has given the name of hemialbumose.

The urine contained a sediment of urates, and an amorphous body, which proved to be hemialbumose. It is probable that the urine being very rich in hemialbumose when it leaves the bladder, deposits it on cooling.

The urine throughout 4—5 weeks was precipitated daily, while fresh, with alcohol, the precipitate washed with alcohol and dried at a low temperature; the product resembled the amber-coloured albumin of commerce. Only part of this preserved hemialbumose was slowly soluble in water. The solution showed all the characteristic reactions, as well as those described by Salkowski. Too much sodium chloride or ferrocyanide prevents precipitation by acetic acid and ferrocyanide of potassium. Excess of sodium chloride and acetic acid produce a precipitate which is soluble on removal of the sodium chloride.

A solution of hemialbumose digested with pepsin at  $40^\circ$  yields peptones only.

Hemialbumose was still extracted from the residue insoluble in water by treatment with 5 per cent. sodium chloride solution. In pure hemialbumose, the author found 0.31 to 1.28 per cent. ash, 0.19 P, 1.09 S in the substance free from ash.

C .....	52.13
H .....	6.83
N .....	16.55

If the hemialbumose solution contain the smallest quantity of acid or alkali, it will not coagulate on heating.

The pure hemialbumose obtained by precipitating with alcohol, dissolving the precipitate in water, and coagulating by warming, has the following properties. Digested with pepsin, peptone only is formed. Digested with trypsin in  $\frac{1}{4}$  to 1 per cent. solution of carbonate of soda after six days, peptone and large quantities of leucin and tyrosin. Boiled with sulphuric acid, leucin and tyrosin are produced. Heated with potash, indol is formed. It will thus be seen that the decomposition products of hemialbumose are the same as those of albumen.

J. P. L.

**Influence of Oat and Wheat Bran on the Secretion of Milk.**

By M. SCHRODT and H. HANSEN (*Bied. Centr.*, 1884, 116—120).—The general outcome of these experiments, in which the cows were fed

with the above substances, in addition to roots and cotton cake, is that there was a marked increase of milk and fat, more especially during the period when oat-bran was given; this excess is attributed to the avenine, which is said to have a strong stimulating action on the lactic glands.

E. W. P.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Production of Ether by the Action of "*Aspergillus Glaucus*" on Lemon-juice.** By T. L. PHIPSON (*Chem. News*, 49, 198).—The author has observed that, when placed in a damp situation, lemons after a certain time develop *Aspergillus glaucus*, and coincidentally emit a strong odour of ether. To explain this phenomenon, it is assumed that ethyl citrate exists in lemon-juice in the same way as ethyl acetate exists in the saps of some plants, or it is suggested as probable that, under the influence of warmth and moisture, fermentation sets up, some of the sugar of the ripe lemon is converted into alcohol, which then combines with the citric acid to form the ethyl citrate; this is ultimately attacked by the *A. glaucus*, and its ethyl groups are evolved as ether. D. A. L.

**Influence of Light and Heat on Plant Development.** By HELLRIEGEL (*Bied. Centr.*, 1884, 123—126).—The temperature during which plant life proceeds is limited within narrow boundaries, there being a boundary for each plant. Near the lowest limit, the growth is very slow, but with rising temperature life becomes more energetic until a certain temperature is reached when the life is most energetic; this temperature is the "optimum," and does not of necessity coincide with the highest temperature at which life ceases. As a rule the optimum temperature lies between 20° and 40°; at 50° life is extinguished. In an analogous manner, light or darkness produces a definite effect, for although germination takes place better in darkness, no plant can grow without light, the plant is bleached, leaves and stems become abnormal, and the weight of dry matter diminishes. In subdued light, assimilation proceeds but slowly, but is more rapid as the intensity of light increases; the maximum of rapidity, however, is not coincident with the maximum intensity of the light. The combination of warmth, light, and moisture form a very important factor in the fertility of the plant, and in many cases it is of more importance than manuring, &c. The lowest limit of temperature at which the majority of seeds can germinate is 4—5°, but a few can germinate at 0°. Experiments were made on various seeds sown in soil kept at different temperatures for 35—60 days. Most of the ordinary seeds germinated below 4°, and winter rye was able to grow at 0°. Wheat germinated and grew at 0°, but hardly so rapidly as rye. Barley and oats required a temperature of 2° to develop, for at 0° they only

developed the radical, and no plumule. Maize required a temperature of  $8.7^{\circ}$ . Linseed developed the radical alone at  $2^{\circ}$ . Vetches only demanded a temperature of  $0^{\circ}$ , whilst peas and clover required  $2^{\circ}$ ; beans and lupines,  $3^{\circ}$ , for the development of the plumule. The lowest temperature for carrots was  $3^{\circ}$ ; for turnips,  $5^{\circ}$ ; and cucumbers showed no signs of germinating at  $8.7^{\circ}$ . E. W. P.

**Influence of Weather on Vegetation.** By F. HILDEBRAND (*Bied. Centr.*, 1884, 138).—An account of the abnormal growth of plants during the remarkable winter of 1882. Here we find annuals flowering and growing during the second year. Biennials, as *Digitalis purpurea*, become shrub-like, plants which flower before their leaves, appear flowering afterwards, and *vice versa*. E. W. P.

**Effect of Water holding Sodium Chloride and Zinc Sulphate in Solution on the Soil and on Plants.** By F. STORP and others (*Bied. Centr.*, 1884, 76—87).—Solutions of sodium chloride cause the loss of greater amounts of sulphuric acid, lime, and potash from soils, the stronger the solution.

The action of this salt as a manure is to decompose the more stable compounds of the soil, but should the amount applied to the land be great, then an excess of calcium and magnesium chlorides are formed, and if in the presence of humus, free acid. To avoid this danger, the manure should be applied only in small proportions, and at a date long previous to that when vegetation should commence. The influence on the composition of grasses is also considerable, for the percentage of albuminoids, dry matter, and fat decrease as the sodium chloride increases. Very dilute solutions ( $\frac{1}{1000}$  per cent.) aid germination, but stronger arrest the process completely.

Soils can absorb as much as 80 per cent. of zinc sulphate from its solutions, and at the same time lose calcium, potassium, sodium, and magnesium compounds; moreover, the loss of potassium increases with the strength of the zinc solution; in the presence of calcium carbonate, zinc sulphate is converted into the carbonate. The preservative action of zinc is exemplified in the neighbourhood of zinc works, where the dust has settled on the pine-needles, and completely prevented their decomposition, but when humic acid is in solution, then the zinc combines with it, and free sulphuric acid is formed.

To an extent similar to that which is found in the case of sodium chloride, zinc sulphate affects the composition of growing grasses, and the ash may contain as much as 2.3 per cent. of the oxide: some plants, as the oak, are but little affected, either by zinc or sodium. The influence on germination is remarkable, for in the dark no harm is done, but in the light it is arrested and the life destroyed; this destructive action does not seem to affect fungoid growths. Experiments in which water containing the two compounds under consideration was allowed to flow over soil, gave results similar to those already mentioned. J. König repeated these last experiments, adding ferrous sulphate, and found that whereas sodium and zinc sulphate reduced the dry matter in the crop, ferrous sulphate raised it; this

result is attributed to the separation of the acid from the base, the acid rendering other material for the plant soluble. E. W. P.

**Respiration of Leaves in the Dark.** By G. BONNIER and L. MANGIN (*Compt. rend.*, 98, 1064—1067).—Comparative experiments respecting the oxygen absorbed and the carbonic anhydride evolved in the dark by the leaves of various species of plants show that the ratio between these two quantities is constant, whatever the temperature, and although the amount of carbonic anhydride evolved increases rapidly with the temperature, the amount of oxygen absorbed increases in exactly the same proportion. The ratio is approximately unity for certain species, e.g., *Euonymus japonicus*, *Aesculus hippocastanum*, whilst for other species, e.g., *Pinus pinaster*, it is considerably less than unity.

The authors have previously shown that the ratio between the carbonic anhydride evolved and the oxygen absorbed is independent of the pressure of the oxygen and of the proportion of carbonic anhydride in the surrounding atmosphere, and it is evident that these two processes of absorption and evolution are most intimately connected.

C. H. B.

**Respiratory Combustion.** By P. SCHÜTZENBERGER (*Compt. rend.*, 98, 1061—1064).—The experiments described in this paper were made with a view to ascertain the effect of the presence of certain organic substances on the respiratory combustion of yeast cells. Similar flasks were filled with equal quantities of water saturated with oxygen, an equal amount of yeast was added to all of them, and then known weights of the particular substances employed, and after the lapse of a given time, the amount of oxygen which had been absorbed was determined by titration. The organic substances added were different varieties of sugar, mannitol, various alcohols, glycerol, acetic, butyric, tartaric, and other acids, sodium acetate, Rochelle salt, and other salts, amido-compounds, hydrocyanic acid, and chloroform. Some of these substances have no appreciable effect on the respiratory combustion, others, such as hydrocyanic acid and chloroform, check it or retard it considerably. Invert sugar, ethyl alcohol, and sodium acetate accelerate the absorption of oxygen in a very marked manner, whilst glycerol and the higher homologues of ethyl alcohol exert a similar but much less energetic action. Methyl alcohol has little or no influence on the process. The effect of the most active substance is equally well observed with fresh yeast, or with yeast which has been exhausted and washed, but the effect of the less active substances is more clearly observed when the exhausted yeast is employed, because the substances naturally present in the fresh yeast are more combustible than those which are added.

The results show that ethyl alcohol is particularly apt to undergo slow physiological combustion, its power in this respect being equal to that of invert sugar. It is possible, indeed, that the invert sugar is first converted into alcohol, and then consumed, and if this be true, ethyl alcohol and the alkaline acetates must be classed in the first rank amongst those substances which undergo combustion in the living organism.

C. H. B.

**Constituents of Vegetable Tissues.** By URBAIN (*Ann. Agronomiques*, 9, 529—547).—This paper contains a *résumé* of the results of Frémy's researches, commenced in 1859 and continued to the present time. The substances composing vegetable tissue are, according to Frémy, the celluloses (cellulose, paracellulose, metacellulose), pectose, vasculose, and cutose.

*Celluloses.*—Cellulose proper, as it exists in cotton and in the utricular tissue of certain fruits, such as the apple, is immediately and completely soluble in Schweitzer's reagent. Paracellulose dissolves in the same reagent only after certain preliminary treatment, such as boiling with very dilute hydrochloric acid. It is found in the epidermic cells of leaves and in root tissue. Metacellulose is insoluble in Schweitzer's reagent, even after treatment with acids. It is not so common as the preceding varieties, and is found principally in fungi and lichens. Like cellulose and paracellulose, it dissolves in strong sulphuric acid without coloration, and can be transformed into glucose. It has also the same elementary composition as cellulose, but differs from it under the action of oxidising agents, and in dissolving in the cold in sulphuric acid, diluted with 4—5 equivalents of water.

It has been objected that the insolubility of crude paracellulose in Schweitzer's reagent is due to the protective influence of earthy or waxy impurities. This is not so, for it remains insoluble even after repeated treatment with alcohol, ether, and alkalis, and even with acids, providing they are cold and dilute. Moreover, it can be rendered soluble by being simply moistened with water and heated in a sealed tube at 125° for several hours.

*Vasculose* is found in almost all the organs of plants, and is particularly abundant in the hard portions. It sometimes constitutes by itself the vessels and tracheæ, and is always the predominant constituent. In the cortical parenchyma and in certain roots, it exists as a continuous membrane. The stony concretions of pears, the stones of fruits, nutshells, &c., contain it in large quantity. It is the "encrusting material" of Payen, but is regarded by Frémy as a definite compound of constant composition and properties, and easy to isolate in a state of purity. One of the easiest modes of isolating it is to remove the cellulose and paracellulose from willow pith by means of sulphuric acid diluted with  $3\frac{1}{2}$  equivalents of water, or by Schweitzer's reagent after previous ebullition with dilute hydrochloric acid. It is a yellowish substance resembling in texture the tissue from which it has been obtained. Sp. gr. 1.5 at 16°. Insoluble in neutral solvents. Not affected by ebullition with sulphuric, hydrochloric, phosphoric, or other dilute acids, or with alkalis. Sulphuric acid diluted with 3.5 equivalents of water (the weakest acid capable of dissolving cellulose) converts it in the cold by abstraction of 2 equivalents of water into a dark brown substance, slightly soluble in the acid, from which it may be precipitated by addition of water.

Nitric acid, chromic acid, alkaline permanganates, and hypochlorites and other oxidising agents act readily on vasculose, converting it into a series of uncrystallisable acids containing more oxygen than the vasculose. Some of these acids are soluble in water and alcohol; others, which are more abundantly formed when the oxidising agent



is weak or acts for a short time only, dissolve only in alkalis. Atmospheric oxygen gradually effects the same changes, hence the decay of wood exposed to air and water. When vasculose is heated at  $130^{\circ}$ , under pressure, with moderately concentrated alkaline solutions, it is rapidly dissolved, furnishing a brown liquor, from which acids precipitate black flocks of complex nature. Part of this precipitate is soluble in ether, part in alcohol, and part in alkalis only. It consists of dehydration-products of vasculose. (The digestion of crude fibre with alkalis in the preparation of pulp for paper-making has for its object the dissolution and removal of the vasculose in this way.) By fusion with potash, vasculose yields similar bodies, the one formed in greatest quantity being soluble in alcohol and strong sulphuric acid, and corresponding in its character with ulmic acid. When submitted to destructive distillation, vasculose yields a considerable quantity of acetic acid and methyl alcohol. Cellulose, on the other hand, yields less acetic acid (always accompanied by formic acid, and a little propionic and butyric acids), and no methyl alcohol. Vasculose contains by analysis  $C = 59.341$  per cent.,  $H = 5.494$ ,  $O = 35.165$ . The formula  $C_{18}H_{20}O_8$  best agrees with its known reactions.

*Cutose*.—The outer layer of the epidermis of leaves and fruits, heated in succession with boiling dilute hydrochloric acid, Schweitzer's reagent, alcohol and ether, for the purpose of removing mineral matter, cellulose and paracellulose, and waxy substances, yields a residue of pure cutose having the composition  $C = 68.293$  per cent.,  $H = 8.953$ ,  $O = 22.754$ .

The cuticle of agave leaves, removed after macerating the leaves in water at  $30^{\circ}$  for some days, answers well for this preparation. Cutose dissolves slowly in boiling dilute solutions of alkalis and alkaline carbonates. Acids precipitate from these solutions a yellowish flocculent substance, fusible below  $100^{\circ}$ , soluble in alcohol and ether, having the same composition as cutose. If the alkaline solution be saturated with common salt, a compound of cutose with the alkali separates and rises to the surface of the liquid as soap does under similar circumstances. When subjected to the action of concentrated solutions of potash for some time, cutose undergoes a somewhat different transformation. The precipitate obtained by saturating the solution with an acid still dissolves in boiling alcohol, but a portion separates out on cooling. The latter, when filtered off, consists of a yellow, solid acid melting at about  $85^{\circ}$ ; after fusion, it is brownish, translucent, and very fusible. The alcoholic filtrate, when evaporated to dryness, yields a brown viscous acid (oleocutic acid). Both of these acids dissolve in ether and in weak alkaline solutions; the alkaline salts are separated from their solutions by excess of alkali or by saturation with salts. The acids combine with strong sulphuric acid in the cold, and can be separated by addition of water, in this respect again resembling the fatty acids. The further action of very concentrated potash solution on the yellow acid above mentioned (or on cutose) results in the production of another acid, in the form of a white translucent potash salt, insoluble in water, soluble in boiling alcohol, but almost entirely reprecipitated on cooling. Hydrochloric acid liberates from this salt *stearocutic acid*, a white solid, melting at  $76^{\circ}$ ;

insoluble in ether and cold alcohol, slightly soluble in boiling alcohol, soluble in hot benzene and hot acetic acid. The yellow acid is a compound of oleocutic and stearocutic acids—stearocutic acid, although almost insoluble in alcohol, dissolves readily in an alcoholic solution of oleocutic acid. Similarly, potassium stearocutate is insoluble in water, but soluble in an aqueous solution of potassium oleocutate.

Analysis of the acids gives the following numbers: Stearocutic acid  $C = 75.000$  per cent.,  $H = 10.714$ ,  $O = 14.286$ , corresponding with the formula,  $C_{25}H_{45}O_4$ , deduced from the composition of its salts; oleocutic acid,  $C = 66.666$  per cent.,  $H = 7.946$ ,  $O = 25.398$ , formula  $C_{14}H_{20}O_4$ . These acids, heated at  $100^\circ$  in presence of water or bases, undergo alteration. Stearocutic acid becomes completely insoluble in alcohol, and its melting point rises from  $76^\circ$  to  $95^\circ$ . Oleocutic acid alters more slowly at  $100^\circ$ , but at  $135^\circ$  it becomes insoluble in ether, alcohol, and hot dilute alkalis. Heated with strong potash, it dissolves and regains its former properties. The yellow compound of the two acids behaves in a similar manner. Cutose is thus a combination of stearocutic and oleocutic acids, in their insoluble modifications, in the proportion of one equivalent of stearocutic acid to five equivalents of oleocutic acid. The action of potash on cutose is to transform the insoluble form of those acids into the soluble form.

Weak nitric acid ( $\frac{1}{2}$  water) transforms cutose into a yellow, waxy nitro-compound, fusible at  $100^\circ$ , soluble in alcohol and alkalis. By further treatment with nitric acid, it is converted into suberic acid. It is the oleocutic acid which gives rise to suberic acid. Suberin, the substance discovered in cork by Chevreul, which by oxidation also gives rise to suberic acid, appears to be the same as cutose, since it yields the same two acids on treatment with alkalis.

*Pectose* is transformed by ebullition with weak hydrochloric acid into pectin, soluble in water, and precipitable by alcohol.

The different behaviour of the substances with various solvents, as described above, has been applied by the author to the proximate analysis of the chief vegetable tissues, with the following results:—

*Stems*, comprising the thin layers of pith parenchyma, wood, and cork.

*Wood*.—The sample reduced to sawdust or shavings is exhausted by alcohol and ether to remove resins, then by distilled water and water made slightly alkaline with potash to remove soluble substances and pectic compounds, and finally with very weak hydrochloric acid, which dissolves the lime and other mineral salts. Oak sawdust submitted to this treatment yields 10 per cent. of water, 4 per cent. substances soluble in alcohol and ether, and 10 per cent. of substances soluble in water and weak alkali. The wood thus purified is treated with Schweitzer's reagent, washed, and dried; the loss is cellulose. It is then boiled with weak hydrochloric acid for a few minutes, and again repeatedly exhausted with Schweitzer's reagent; the loss this time being paracellulose. The residue is pure vasculose. Purified oak sawdust treated in this way yields in 20 grams 5.41 grams cellulose, 8.58 paracellulose, and 6.01 vasculose; poplar yields in 20 grams

6·82 cellulose, 9·19 paracellulose, and 3·99 vasculose. These results are confirmed by dissolving out the two varieties of cellulose together by sulphuric acid, and weighing the residual vasculose; also by removing the vasculose by treating the sawdust with nitric acid ( $\frac{1}{2}$  water) in the cold, boiling with ammonia, and weighing the unacted on residue of celluloses. Some varieties of wood, *e.g.*, boxwood, yield no cellulose when analysed, as they are composed entirely of vasculose and paracellulose. The following table shows the percentage composition of six kinds of wood:—

	Vasculose.	Cellulose and paracellulose.	Water and extractives.
Poplar .....	18	64	18
Oak .....	28	53	19
Box .....	34	28	38
Ebony .....	35	20	45
Guaiacum .....	36	21	43
Ironwood .....	40	27	33

*Pith parenchyma* is made up of the same constituents as woody tissue, and is analysed in the same way. Purified elder pith, *e.g.*, contains cellulose 37 per cent., paracellulose 38, vasculose 25.

*Cork* contains cutose in addition. After purification, the cutose is directly dissolved out by boiling potash, and is estimated by loss of weight. The residue is analysed in the same manner as wood. Common cork has the following percentage composition:—Water 2, soluble in ether and alcohol 9; soluble in water, weak ammonia, and weak hydrochloric acid 5; cutose 43, vasculose 29, cellulose and paracellulose 12.

*Roots*.—Root tissue is composed of paracellulose, vasculose, and often pectose also. The vasculose forms a continuous membrane over the root surface, and constitutes the chief part of the root vessels. Pectose may be dissolved out of the purified tissue by boiling with weak hydrochloric acid, after which the vasculose and cellulose are separated as indicated above. A root of *Paulownia* gave the following results:—

	Outer layer.	Soft fibre (liber).	Body of root.
Water .....	8·35	6·64	6·00
Substances soluble in water, alcohol, &c.....	10·40	—	26·25
Extractive matters and pectose	—	55·70	—
Ulmic compounds soluble in potash .....	33·15	—	—
Substances soluble in ammonia and weak HCl .....	—	—	21·00
Vasculose .....	44·40	34·25	17·30
Paracellulose .....	3·70	3·41	29·45
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

*Leaves.*—The parenchyma, chiefly cellulose, may be separated from the epidermis and from the fibres and vessels by maceration in water, or by Schweitzer's reagent.

The *epidermis* is composed of two membranes closely united; the outer one (cuticle) is formed of cutose, the inner one of paracellulose. The paracellulose can be dissolved away from the cutose by treatment with Schweitzer's reagent after boiling with dilute hydrochloric acid, or by treatment with sulphuric acid + 3·5 equivalents of water. Or the cutose may be dissolved away by boiling potash, or by treatment with cold nitric acid, followed by an alkaline solvent. Ivy leaves yielded the following figures:—

Water and substances soluble in water,		
alcohol, and ether .....	90·77	
Parenchyma (cellulose and pectose)...	4·00	
Fibres and vessels {	vasculose .... 0·95	} ... 1·73
	paracellulose.. 0·78	
Epidermis {	cutose ..... 1·05	} .... 3·50
	paracellulose.. 2·45	
		<hr/> 100·00

*Flowers.*—Petals have the same constituents as green leaves. They are first boiled with alcohol to remove waxy substance and colouring matter, and then analysed like leaves. Dahlia petals contain—

Water, and substances soluble in water,	
alcohol, and ether .....	96·130
Parenchyma (cellulose and pectose) ..	3·163
Cutose .....	0·360
Vasculose .....	0·120
Paracellulose .....	0·227
	<hr/> 100·000

*Fruits.*—The *epicarp* of fruits, such as apples, pears, &c., consists of three superposed membranes: the outside one consisting of cutose, the intermediate one of vasculose, and the inside one of paracellulose. They can be separated by the reagents already mentioned.

The composition of the *endocarp* is similar to that of wood, and the analysis is executed in the same manner. Vasculose predominates, and the hardness varies according to the quantity of this substance present—

	Vasculose.	Cellulose and paracellulose.	Water and extractives.
Walnut shells .....	44	25	31
Hazel nut shells ....	50	31	19
Cocoanut „ ....	58	25	17
Apricot stones .....	60	26	14
Bankoul nuts.....	62	14	24

The cells of the *mesocarp* consist of cellulose and pectose, and when

the latter of these is removed by ebullition with water, acidulated with hydrochloric acid, and the former by Schweitzer's reagent; nothing is left but the vessels and tracheæ formed of vasculose and paracellulose.

In the seed, the perisperm, after removal of starch, oils, &c., consists entirely of cellulose; whilst the integuments contain vasculose, cutose, cellulose, and paracellulose.

J. M. H. M.

### Phenol in the Stem, Leaves, and Cones of *Pinus Sylvestris*.

By A. B. GRIFFITHS (*Chem. News*, 49, 95).—The author has detected and estimated phenol in aqueous decoctions of the stem, leaves, and cones of *Pinus sylvestris*. The various parts are cut into small pieces and digested at 80° for half an hour, with successive quantities of water, until the filtered solution gives no coloration with ferric chloride; it is then evaporated and extracted with ether, &c. The quantity of phenol found in the separate parts varies according to their age; thus: old stem contains 0·1021, whilst young stem contains only 0·0654 per cent. The variation with the leaves is from 0·0936 down to 0·0315 per cent., whilst the amount in the cones varies from 0·0774 to 0·0293.

This result, coupled with the existence of phenol in coal, is adduced in support of the presumed existence of *coniferae* in the carboniferous age; and, moreover, taking into consideration the many hydrocarbons, &c., common to both coal and petroleum, the author argues that petroleum also is of vegetable origin.

D. A. L.

**Chemical Investigations on the Kola.** By E. HECKEL and F. SCHLAGDENHAUFFEN (*Ann. Chim. Phys.* [6], 1, 129—138).—The extract of the kola-nut, from a plant of the Sterculiaceæ family, is used as a beverage by the inhabitants of Central Africa, as tea or coffee by the Asiatics and Europeans, or maté by the Americans. As few specimens of the plant have come to Europe, investigations on the chemical nature and therapeutic functions of the extract have been incomplete; but the experiments of Daniell and Attfield have proved the presence of an alkaloïd resembling that from tea or coffee. From the opening out of commercial routes into Central Africa considerable quantities of the true kola or *Kola femelle*, and of its principal substitute, Kola bitter, have been shipped into France.

*Kola Femelle* (*Sterculia acuminata*).—On extracting the kola-nut with chloroform, an alkaloïd is obtained resembling caffèïne in all its properties, together with smaller quantities of theobromine.

The results of the analyses are as follows:—

	Per cent.
Extracted by chloroform	Caffeïne . . . . . 2·348
	Theobromine . . . . . 0·023
	Tannin . . . . . 0·027
	Fats . . . . . 0·585
Extracted by alcohol	Tannin . . . . . 1·591
	Kola red . . . . . 1·290
	Glucose . . . . . 2·875
	Salts . . . . . 0·070

	Per cent.
Starch.....	33·754
Gum .....	3·040
Colouring matters.....	2·561
Protein .....	6·761
Ash .....	3·325
Water .....	11·919
Cellulose.....	29·830

On comparing these results with the analyses of cacao, tea, and coffee, it is noted that kola contains a considerably larger proportion of carbohydrates and their derivatives, and also of caffeine and its homologue theobromine. Kola extract should therefore be a valuable therapeutic agent.

*False Kola or Kola Bitter (Kola garcinia).*—In Liberia and Central Africa, a plant of the family of the Guttiferæ grows in abundance, producing a grain known by the name of kola bitter. On extracting this with chloroform, ether, and alcohol, no caffeine was obtained, but only resins, of which one gave a violet coloration with ferric salts; the other in aqueous solution was dextrorotatory, and precipitated by tartar emetic and basic lead acetate. The physiological action of the extract of this grain is attributable to the presence of these two resins.

V. H. V.

**Sterilisation of Liquids by Means of Papin's Digester.** By L. HEYDENREICH (*Compt. rend.*, 98, 998—1000).—When flasks containing liquids, &c., are introduced into a Papin's digester, the air should be removed as completely as possible, for if this is not done it forms a protecting layer or cushion round the flask or other vessel, and prevents the contents of the latter from attaining the temperature of the water in the digester. From this cause the temperature of the contents of the flask may be but little higher than 60°, even after the temperature of the digester has been at 120° for some time. If, however, care is taken to remove all the air, the contents of the flask quickly acquire a temperature practically as high as that of the water in the digester.

C. H. B.

**Silage.** By G. TOMS (*Bied. Centr.*, 1884, 136).—Composition of heated hay: Fat = 4·26 per cent., trace of aldehyde, acetic acid 5·38, sugar 6·94, starch 3·42, mucilage, &c., 24·77; in the same hay that had not heated was starch = 12·46. Other samples of silage were brown, of bad odour, and contained more acid and less starch.

E. W. P.

**Woody Fibre as Fodder.** By M. MÄRCKER (*Bied. Centr.*, 1884, 136).—Wood is not digested by animals, for although it does not appear in the dung, it is converted for the most part by fermentation into marsh-gas.

E. W. P.

**White Mustard as Fodder.** By BRÜMMER (*Bied. Centr.*, 1884, 115).—White mustard is strongly recommended as green food, and

should be mixed with chaff, &c., because of its highly nitrogenous composition. It produces very highly coloured butter.

E. W. P.

**Champion Spice.** By C. O. HARZ (*Bied. Centr.*, 1884, 122).—The origin of this spice, which is much used as an addition to cattle food, appears to be the waste from drug stores, factories of ethereal oils, &c., mixed with palm-nut cake, &c. The price is excessive, its feeding value but low, and its purchase not to be recommended. Its chemical composition has been already given in a previous number, but the following is its botanical constitution in parts per 1000: Ginger 40 parts, inula root 24, caroba bean 120, corianders 80, fennel 120, aniseed 80, carraway 40, fenugreek seeds 168, turmeric 120, palm-nut cake 68, maize 40, cereals 40, rice 8, peas, vetches, and hog's bean 4, dirt, &c., 40.

E. W. P.

**Varieties of Sugar-beet.** By M. MÄRCKER (*Bied. Centr.*, 1884, 126).—Of the many varieties of beet grown, the Simon Legrand de Mères Blanches yielded the largest number of centners of sugar per morgen (28·2), but its quotient of purity was 83·4, whilst that of Vilmorin Blanche was 85·8 with a yield per morgen of 23·61. Bestehorn's Imperator was the poorest, 23·52 centners, quotient = 82·4.

E. W. P.

**Manuring Potatoes.** By M. MÄRCKER (*Bied. Centr.*, 1884, 102—104).—The object of the experiments was to determine the best form in which to apply nitrogen, the extent to which potash salts do harm, the value of superphosphate as compared with fæcal superphosphate, and the best proportions in which to mix nitrogen with phosphoric acid. The soil on which the experiments were first made was sand, containing hardly any plant food, and quite uncultivated, and here it was found that a larger supply than 8 kilos. N and 10 kilos.  $P_2O_5$  per morgen, brought no relatively higher yield. Ammonia with superphosphate was qualitatively and quantitatively better than Chili saltpetre; the addition of large quantities of potash salts in the spring further lowered the quality, the first reduction having been caused by the Chili saltpetre. Superphosphate of organic origin was more valuable than that of mineral origin; ammonia produced as large an increase as Chili saltpetre did a reduction. The second set of experiments with the object of determining the effect of potash on the percentage of starch was made on very light but well cultivated soil; in previous years, potash put in in the spring had a lowering effect on the starch, therefore potash and other artificials were now added in the autumn. The results obtained were very definite, and are as follows: the appearance of the crop is much improved by the addition of the potash salts in the autumn instead of in the spring, moreover the percentage of starch is increased: the qualitative and quantitative yield of tubers is highest when the ratio of nitrogen to soluble phosphate is  $7 : 9\frac{1}{2}$ ; as a rule, as this ratio widens, so is the phosphate less employed: the application of potash alone is distinctly detrimental to the crop, in fact, lowered it below the unmanured plot. The third series was made on light sandy soil,

which had been brought into cultivation by peat and farmyard manure; the half of this land was also treated with 2 centners kainite in autumn, one-quarter received kainite in spring, whilst the remaining quarter was left without kainite. In the previous year, we find that the spring manuring reduced both the quantity and the quality, but this year the quality alone was affected; the organic superphosphate was better than the inorganic. The ratio  $N : P_2O_5 = 7 : 9.5$  was again found to be the most favourable. The autumn manuring with kainite produced a larger crop, but of lower quality than in the previous season, and this mineral by itself was again distinctly detrimental; if the application of potash during the autumn regulates the yield of starch, then the best result under the circumstances is obtained when  $N : P_2O_5 = 5 : 7.5$ . Although kainite has such an unfavourable action, yet, on the other hand, by its use the plants resist more easily the attacks of disease, and the tubers are more generally normal in form and keep better. E. W. P.

**Manuring Potatoes.** By C. A. CAMERON (*Bied. Centr.*, 1884, 104—106).—No statement of the character of the soil is given, but remarkable is the yield produced by kainite (736 kilos. per hectare), when the highest absolute yield at the lowest cost was obtained, also we find an advantage gained by the use of this manure in combination; superphosphate with Chili saltpetre brought the largest amount of marketable potatoes, but when mixed with ammonia the result was bad. Nitrogenous manures alone were very unsatisfactory, the yield being below that of the unmanured plot; and even when mixed, these manures were of doubtful advantage as regards quantity, but otherwise as regards quality, as by their use but few diseased tubers were produced. The highest percentage (28.6 per cent.) of dry matter was produced by the aid of nitre and superphosphate, whilst kainite yielded the lowest (24.3 per cent.). E. W. P.

**Salt and Herring Offal as Manure.** By E. D'ORVAL and A. PAGNOUL (*Bied. Centr.*, 1884, 92—98).—Mixed with earth-nut meal or guano, sodium chloride seemed to produce no further effect than when the two first manures were employed alone. A well-marled field was manured with 3000 kilos. per hectare of herring offal, and then sown with wheat home grown on part, on the other part "golden drop"; on neighbouring fields sown on the same day, but manured with farmyard manure and poudrette, the wheat seeded a fortnight earlier than when the offal had been used, moreover this material had a very depreciating effect on the yield of grain and straw. In the succeeding season, superphosphate was added, and rye and vetches sown; this crop showed that the harmful matter had been removed from the offal, and a good yield was the result. Another trial with oats was also successful on the first season; three experiments show that there is a very considerable variation in the effect exerted by the salt in the offal on the ordinary crops, for native wheat was harmed but little; peas, beans, and English wheat suffered heavily, but oats only during the germinating period; when treated with water so as to remove excess of salt, not much phosphoric acid is lost, but a loss of nitrogen



occurs (0·7 per cent.), and from the wash water, ferric chloride, and lime throw down a precipitate containing 2·8 per cent. N. The washed offal is priced at 12 m. per centner, and is a valuable manure, and would be more so if the fat were removed. E. W. P.

**Production and Cost of Farmyard Manure.** By HOLDEFLEISS and M. HERTER (*Bied. Centr.*, 1884, 87—92).—The composition of four samples of fresh manure produced by 70 head of cattle, fed in boxes, was—dry matter 27·5 per cent., N = 0·666,  $K_2O$  = 0·877,  $P_2O_5$  = 0·222; these quantities are in close accordance with those obtained by calculating the amount which after digestion should be produced, in addition to the straw (15 lbs. rye-straw per head), and the reduction in weight of the manure after lying in heaps; the calculated composition is—N = 0·617,  $K_2O$  = 0·858,  $P_2O_5$  = 0·299. The values of the constituents of such a manure are 1 lb. (German) = 0·80 m., 1 lb.  $K_2O$  = 0·18 m., 1 lb.  $P_2O_5$  = 0·20 m., consequently 20 centners = 22·05 m. The advantages of feeding in boxes are here set forth: no loss of urine, more straw can be worked into manure, and the whole is better made than otherwise.

Herter shows the balance sheet of a dairy farm, which, when account is taken of milk, butter, and cheese produced, the expenses of attendance, &c. (not fodder), shows a nett income of 263 m. per cow. The value of the food given in winter is 203·7 m., in summer 82·5, total 286·2 m. per 1000 lbs. live weight. According to these figures, the costly feeding neutralises the value of the cow and raises the value of the manure to 48 m. per 20 centners. E. W. P.

**Manuring with Sea-mud and Peat Compost.** By ENCK-HAUSEN (*Bied. Centr.*, 1884, 100—102).—On light sandy soils, or on poor land underlaid by a cold subsoil, sea-mud is better than stable manure. A compost was made of mud, farmyard manure, phosphorite, kainite, and sawdust, and contained N = 0·34 per cent.,  $P_2O_5$  (soluble in cold acid), 0·21 per cent. When this mixture was applied to oats and potatoes, the result was very satisfactory, and when compared with farmyard manure, was found to be much cheaper; in fact, the use of the latter with oats did not produce grain sufficient to pay the extra cost. E. W. P.

**Superphosphate.** By F. J. LLOYD (*Chem. News*, 49, 229—230).—In the annual reports of the experiments of the Sussex Agricultural Association, certain anomalous and detrimental effects are described, and attributed by Jamieson to the superphosphate employed as manure; therefore, superphosphate is denounced as not alone unnecessary, but also injurious. Now, from the analytical data supplied in these reports, it is shown, in the present note, that the superphosphate employed in the experiments in question differed from the ordinary superphosphate of commerce in having a very large excess of free sulphuric acid. This probably accounts for the bad results referred to.

D. A. L.

**Assimilability of the Phosphoric Acid in Rocks and Soils.**

By G. LECHARTIER (*Compt. rend.*, **98**, 1058—1061).—The schists and granites employed were crushed, washed to remove organic matter, dried, and finely powdered. A series of pots was filled with the powdered rock mixed with an inorganic manure containing nitric and ammoniacal nitrogen, calcium sulphate, potash, and phosphates, and a second series was filled with a similar mixture, except that no phosphate was added, and buckwheat was sown in all the pots. The influence of the phosphates in the manure was very marked; but in all cases the plants in the pots containing the manure free from phosphates, assimilated a certain quantity of phosphoric acid from the powdered rock. The schists and granites employed contained phosphoric acid in proportions varying from 0.108 to 0.207 per cent.; but in most cases fluorine was also present, so that the phosphoric acid may have existed, in part at least, as apatite.

The phosphates contained in the schists and granites are partly soluble in dilute acetic acid (1 : 5), or a 2 per cent. solution of ammonium oxalate; and since the latter reagent also dissolves a certain proportion of potash, and of the humous substance which can be separated by Grandeau's process, it may be used as a means of determining the degree of solubility of the fertilising constituents of a soil.

Small quantities of phosphoric acid are not precipitated by ammonium molybdate in presence of ammonium oxalate; the latter should therefore be removed by evaporation and ignition. C. H. B.

**Kainite and Bone-meal in Sandy Soil.** By F. W. STEFFENS (*Bied. Centr.*, 1884, 99).—Rye was sown after one year's clover-ley which had been ploughed in, and 3 centners kainite with 1 centner bone-meal were added at the time of sowing; the gain over unmanured soil was equal to 25 m. per morgen. Bone-meal, without kainite, was unsatisfactory. E. W. P.

**Carnallite, a Cheap Substitute for Kainite.** By TROSCHSKE (*Bied. Centr.*, 1884, 98).—It is here stated that kainite is nearly twice as costly as carnallite, whilst the properties of the latter surpass those of the former: for example, to absorb 1 kilo. ammonia the expenses are as 44 : 13, so that carnallite may be well employed in stalls to soak up urine. Again, atmospheric ammonia is absorbed to the extent of 9 per cent. by carnallite, 4.5 by kainite. The reckoning on the other side against carnallite is, that the magnesium chloride it contains is not good for plants; at least not to be recommended for roots and potatoes. E. W. P.

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## Analytical Chemistry.

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**Litmus, Rosolic Acid, Methyl-orange, Phenacetolin, and Phenolphthaleïn as Indicators.** By R. T. THOMSON (*Chem. News*, 49, 119—121; compare this vol., 691).—The present paper contains further notes to the previous communications already referred to (*loc. cit.*).

*Determination of Small Proportions of Hydroxide in presence of Large Quantities of Carbonates and other Compounds of Sodium and Potassium.*—The process described is founded on the neutrality of precipitated barium carbonate to phenolphthaleïn; and, employing this indicator, it consists in adding excess of neutral barium chloride to the solution of sodium or potassium carbonate, in which the amount of hydroxide is to be determined, then after the further addition of a little more of the same indicator, titrating the hydroxide in solution with standard acid. The whole process must be conducted in the cold, as heating gives rise to low results. The efficiency of the process is proved by test experiments. The barium chloride cannot be replaced effectually by a calcium salt. Impurities such as chlorides, sulphates, and sulphites, do not interfere with this method, nor do phosphates to any appreciable extent; whilst sulphides may be rendered harmless by treatment with a few drops of hydrogen peroxide. With aluminates, the whole of the alkali is determined, but with silicates, only 90 per cent. of it.

The process may evidently be applied to similar determinations in other salts yielding precipitates with barium neutral to phenolphthaleïn, *e.g.*, normal sulphites and phosphates. By the following scheme, the amount of sodium or potassium sulphite, carbonate, hydrogen carbonate, or hydroxide may be determined in a few minutes. The hydroxide is estimated as already described; then by titrating another portion in the cold, using phenolphthaleïn, the hydroxide and half the carbonate is found; and finally, using methyl-orange, and a further addition of acid, the other half of the carbonate and half the sulphite is obtained. From these data, the various proportions are easily calculated.

*Determination of Sodium or Potassium Hydrogen Carbonate in presence of Normal Carbonate.*—This is another application of the above process. The solution under examination is mixed with excess of standard caustic soda, in which the hydroxide has been determined by the above method; barium chloride is added, and the excess of hydroxide employed titrated with standard acid; the difference between this quantity and the total soda used gives the amount required to neutralise the hydrogen carbonate. Successful test experiments show the value of this method.

*Behaviour of Sodium and Potassium Arsenates.*—With *litmus*, *rosolic acid*, and *phenacetolin*, the change in colour is gradual and the end-reaction indistinct. *Methyl-orange* changes colour suddenly at the finish, although the full pink is not developed until there is a slight

excess of acid. With *phenolphthaleïn*, on the other hand, the neutral points at different stages, as well as the end-reaction, are well defined. The following results have been obtained:—

$\text{Na}_3\text{AsO}_4$  used for each test, 2.08 grams (=  $\text{Na}_2\text{O}$  = 0.93 gram).

Indicator.	c.c. normal acid consumed.	Grams $\text{Na}_2\text{O}$ found.
Litmus.....	19.90	0.6169
Rosolic acid .....	19.85	0.6154
Methyl-orange .....	20.0—20.05	0.6200—0.6215
Phenacetolin .....	19.90	0.6169
Phenolphthaleïn, cold ....	10.0—10.00	0.3100—0.3100
„ „ hot ....	10.9—11.00	0.3379—0.3410

from which it will be seen that disodium hydrogen arsenate is neutral to phenolphthaleïn, whereas sodium dihydrogen arsenate is neutral to the other four. Therefore, the amount of *arsenic acid in an alkaline arsenate may be determined* as follows:—Dissolve the sample in water, filter, neutralise with methyl-orange as indicator, boil off carbonic anhydride, cool, add phenolphthaleïn, and determine with normal or  $\frac{N}{2}$  sodium hydroxide. Sodium carbonate does not interfere with this change, sodium arsenite does, but this compound is seldom present in commercial arsenate, for which this method is intended.

With *Sodium and Potassium Arsenite, litmus, rosolic acid, and phenacetolin*, change slowly, but give a distinct end-reaction; *methyl-orange* is as good as with carbonate, whilst *phenolphthaleïn* indicates too soon. The results obtained, using 1.30 grams  $\text{NaAsO}_2$  = 0.31 gram  $\text{Na}_2\text{O}$  for each test, were:—

Indicator.	c.c. normal acid used.	Grams $\text{Na}_2\text{O}$ found.
Litmus.....	10	0.310
Rosolic acid.....	10	0.310
Methyl-orange .....	10—10	0.310—0.310
Phenacetolin .....	10	0.310
Phenolphthaleïn, cold ....	9.05—9.1	0.2805—0.2821
„ „ hot ....	8.90—9.0	0.2759—0.2790

Arsenious acid is neutral to methyl-orange; but, as will be seen, it requires a large quantity of alkali to make it neutral to phenolphthaleïn: hence its interference in the determination of arsenic acid. Similar experiments on the determination of boric acid in borates have not yielded satisfactory results. D. A. L.

**New Volumetric Method for the Estimation of Nitrous Acid.** By A. G. GREEN and S. RIDEAL (*Chem. News*, 49, 173—174).—The method recommended by the authors is founded on the action of nitrous acid on aniline; the formation of diazo-benzene takes place quite quietly and quantitatively, provided due precautions are observed. The following is the method adopted for applying this reac-

tion to the quantitative determination of nitrous acid:—A decinormal solution of aniline is prepared with slightly more than twice its equivalent of acid, one-half being sulphuric and the other hydrochloric acid. A weighed quantity of nitrite is dissolved in sufficient water to make the solution between deci- and centi-normal. A rough determination of the nitrous acid in the sample is now made with centi-normal permanganate, or the aniline solution: and then several experiments are started, employing varying quantities of nitrite approximating to the number found above, along with the same quantity of aniline solution. After remaining overnight (if great accuracy is required in an atmosphere of carbonic anhydride), an equal volume of starch and potassium iodide solution is added to each, which speedily indicates even a very small excess of nitrous acid in any of the experiments, thus showing where too much nitrite was used. Estimations of nitrous acid have been made by this method to less than 0.1 per cent.: moreover, it can be employed where permanganate is inadmissible from the presence of reducing agents.

D. A. L.

**Estimation of Nitric Acid.** By E. WILDT and A. SCHEIBE (*Zeitschr. Anal. Chem.*, 1884, 151—157).—The authors have constructed a combination of apparatus which admits of the employment of Schloesing's well-known method without the use of mercury, the nitric oxide formed being reoxidised into nitric acid and determined acidimetrically. The test experiments quoted are very satisfactory, and the working of the method, which requires the aid of a diagram for its elucidation, is quite simple.

O. H.

**Estimation of Phosphoric Acid.** By G. H. OGSTON and others (*Chem. News*, 49, 230—231).—The following directions are given as a step towards getting uniform results when phosphoric acid is determined in the same material by different operators. 1. Two samples should be supplied by the manufacturers, one very finely divided, the other coarsely crushed. 2. The phosphoric acid is to be determined in the ground sample dried at 100°, the moisture in the crushed sample, and, if desired, in both samples. 3. In event of the results obtained by two experimenters differing by more than 1.5 per cent., their opinion is to be asked as to the cause of the difference.

D. A. L.

**Estimation of Phosphoric Acid in Arable Soils.** By DE GASPARIN (*Compt. rend.*, 98, 963—964).—The author admits the truth of Lechartier's statement, that in his method (*Abstr.*, 1883, 619) the whole of the phosphoric acid is not extracted from the calcined residue by treatment with dilute nitric acid. The phosphates should be precipitated by ammonia, dissolved in nitric acid *without calcination*, and the phosphoric acid precipitated by ammonium molybdate. In presence of a considerable proportion of alkaline earths, the calcination method gives accurate results.

C. H. B.

**Estimation of Boric Acid on Borosilicates.** By C. BODEWIG (*Zeitschr. Anal. Chem.*, 1884, 143—149).—Such minerals are generally

fused with an alkaline carbonate, the mass extracted with water, and in the solution the silicic acid is for the most part precipitated by the addition of ammonium chloride or carbonate. The silica still remaining in solution is precipitated, after the removal of all ammonium carbonate, by a solution of zinc oxide in ammonia. This latter treatment must be repeated, but a little boric acid appears to enter into the precipitate. The author therefore proposes to omit the precipitation with zinc oxide, and to estimate the small amount of silica still remaining in the subsequently obtained borate precipitates, that is, in the magnesium borate (Marignac's method), or in the potassium borofluoride (Stromeyer's method).

E. F. Smith has described (*Amer. J. Sci.*, 1882) a volumetric method of estimating boric acid. He precipitates the borate solution with excess of standard manganous sulphate, filters, and estimates the excess of manganese in the filtrate by potassium permanganate. E. F. Smith fuses insoluble borates with sodium carbonate, adds to the solution of the melted mass an excess of ammonium sulphate, heats until all ammonia is expelled, and then titrates the solution as described. According to Bodewig this method is quite incapable of furnishing even approximate results. O. H.

**Estimation of Quartz in Siliceous Rocks and Soils.** By J. HAZARD (*Zeitschr. Anal. Chem.*, 1884, 158—160).—The exceedingly finely powdered silicate is heated for six hours with 2 parts of concentrated sulphuric acid and 1 part of water at 250°, the insoluble residue washed with water, caustic alkali, and hydrochloric acid.

The author has ascertained that the following silicates are completely decomposed by sulphuric acid:—Muscovite, biotite, garnet, tourmaline, talc, hornblende, hypersthene, diallage, and pyroxene, and of the felspars labradorite and anorthite, whilst albite, orthoclase and oligoclase are not attacked. The residue obtained as described may therefore contain one or more undecomposable silicates. In it therefore the amount of alumina and of lime is estimated, and from the data obtained the proportion of silicates calculated.

For 1 part of lime found in the residue, the author subtracts from the total alumina 1.8321 parts of  $\text{Al}_2\text{O}_3$ , and for each part of this 1.1696 from the  $\text{SiO}_2$ . Of the  $\text{Al}_2\text{O}_3$  left, each part corresponds to 3.5088 parts of combined  $\text{SiO}_2$ ; the remainder is quartz. O. H.

**Estimation of Cuprous Chloride in Copper Liquors.** By S. G. RAWSON (*Chem. News*, 49, 161—162).—In the extraction of silver from pyrites by Claudet's method, large quantities of cuprous chloride are prejudicial, because the zinc iodide employed instead of only precipitating the silver, is partially used up for the formation of cuprous iodide. It is therefore important to determine the quantity of cuprous chloride in copper liquors, and for this purpose the only satisfactory method is treatment with ferric chloride (which is reduced to ferrous) and titration with permanganate. Copper liquors generally contain cupric, cuprous, sodium, silver, and ferrous chlorides, free hydrochloric acid, zinc, calcium, lead and sodium sulphates, an insoluble residue,

and of course water. It is shown that although the amount of acid added when standardising the permanganate either with ferrous sulphate or iron dissolved in sulphuric acid, does not affect the result, nevertheless the amount of ferric chloride and sulphuric acid added in the titration of cuprous chloride, does alter the result to a considerable extent, in fact, the results increase directly with the quantities of either of these reagents employed. This irregularity is proved to be due to the liberation of hydrochloric acid, and for this reason the author suggests the use of ferric sulphate instead of ferric chloride for these determinations. The ferric salt is best dissolved by making into a paste with sulphuric acid, and then mixing with cold water. Of course the ferrous chloride in the copper liquors is determined from time to time.

D. A. L.

**Volumetric Estimation of Iron.** By R. W. ATKINSON (*Chem. News*, 49, 117—119, and 217—218).—In this communication, the direction is pointed out and experimentally illustrated, in which certain quantitative errors in the volumetric estimation of iron may originate. Firstly, during the preparation of the standard solution, and secondly, in standardising this solution. For the preparation of standard dichromate, the salt should not be fused, but the pure salt should be finely powdered, and dried in a steam-oven previous to use. With regard to standardising, it is observed that very different results are obtained, according to the form of iron employed for this purpose. Of materials employed in such case, ferrous sulphate is out of the question; ferrous ammonium sulphate, when pure, will remain constant in composition for several months, but is ultimately liable to alteration; ferric oxide is very good for standardising, but it is very difficult to obtain in a pure state, owing to the facility with which it becomes contaminated during its preparation; on this account, steel of known composition is generally employed, dissolved either in dilute sulphuric, or nitric acid, and in the latter case the nitric acid is eliminated by evaporating the solution to dryness with hydrochloric acid; the residue is then taken up with hydrochloric acid, the solution neutralised, reduced with ammonium hydrogen sulphite, and the sulphurous acid got rid of by treatment with dilute sulphuric acid and boiling. The author has made several series each of many experiments, testing the dichromate solution with ferrous ammonium sulphate, with steel dissolved in dilute sulphuric acid, and with steel dissolved in nitric acid and treated as described above.

The final average results are as follows:—

	I.	II.	III.
Potassium dichromate solution.	With ferrous ammonium sulphate.	Steel dissolved in sulphuric acid.	Steel dissolved in nitric acid.
1 c.c. = Fe	0.0053986	0.0053656	0.0053994

From which it is obvious that whereas the results I and III agree very well, result II differs from both by 0.000033 or more, which could amount to a loss of 0.3 per cent. Fe in a determination; therefore steel dissolved in sulphuric acid should not be used for standard-

ising. The low result is probably caused by the presence of the carbonaceous matter of the steel in the sulphuric acid solution, exerting a reducing action on the dichromate, whilst by treatment with nitric acid and evaporating, this matter is destroyed.

In this first part of the paper, the author discusses the preparation and standardising of the potassium dichromate solution for the volumetric determination of iron, and thus fixes a trustworthy standard: the second part treats of the methods used in the titration.

Of course the ore is pulverised as finely as possible, and is thoroughly dried and accurately weighed. It is dissolved by prolonged digestion with hydrochloric acid. In the present instance there was no evidence to show that ferric chloride is volatile at  $100^{\circ}$ . The next step is to reduce the solution of the ore, which is done either with zinc, or stannous chloride, or sulphurous acid.

*Zinc* can be used successfully only when it is free from or contains a known quantity of iron. There are, however, other objections to its use, namely, it dissolves but slowly, and secondly, the zinc chloride in solution retards the development of the blue coloration when testing with potassium ferricyanide, both these objections tend unnecessarily to prolong the time of analysis; finally, the end blue reaction is so indistinct that as much as from 0.1 to 0.2 per cent. of the iron in the ore may be overlooked. Consequently, although the zinc method may yield uniformly concordant results, it cannot be regarded as extremely accurate.

The *stannous chloride* method is fully described and most emphatically denounced, inasmuch as it is not only extremely difficult to get accurate results, but the ultimate result is in the hands of the analyst; for owing to the fact that, after adding excess of stannous chloride to effectually reduce the iron in solution, it is necessary to oxidise the unused reagent before proceeding with the titration of the iron, it is obvious that either insufficient oxidation, or too liberal oxidation of this unused stannous chloride must most seriously impair the result.

The most trustworthy method of reduction is with ammonium hydrogen sulphite, which is conducted in the following manner:—The solution of ore is diluted with acidulated water, filtered, neutralised with ammonia, and the slight precipitate of ferric hydroxide redissolved by a few drops of hydrochloric acid. Strong ammonium hydrogen sulphite solution is now added (about 1 c.c. for each 0.1 gram of ore employed), the solution well shaken, and boiling water added. It is now acidified with dilute sulphuric acid (1 to 6), and after boiling for half an hour the solution is titrated with dichromate. Numerous experiments show that by following these directions, constant and accurate results can be obtained. The advantages are that the most stable ferrous compound, ferrous ammonium sulphate, is dealt with, and moreover the ferricyanide reaction is decided and delicate, detecting a difference of 0.00025 gram iron. The decomposition of the ferricyanide solution may be retarded by protecting it from light. A mixture of ferric chloride and potassium ferricyanide is reduced by exposure to light, and therefore blue colour is developed; this is important in testing; it is hence advisable to shade the testing slab during use.

D. A. L.



**Estimation of Phosphorus in Iron and in Iron-ores.** By A. TAMM (*Chem. News*, 49, 208—210).—In the present memoir an account is given of systematic investigations on some of the methods employed for the determination of phosphorus in iron and iron-ores, conducted by the author with the assistance of some other chemists. With regard to dissolving the iron previous to the precipitation with ammonium molybdate, the following method is recommended as the best:—The iron is dissolved by boiling with nitric acid, sp. gr. 1.20, using 12 c.c. for each gram of iron taken, the solution is boiled briskly to dryness, and the dry iron salt after heating for one hour at about 200° (or the melting point of tin), is dissolved in hydrochloric acid, sp. gr. 1.19, employing 6 c.c. for each gram of iron. The solution is again boiled quickly to dryness, taken up as before with hydrochloric acid, and the excess of acid evaporated as far as possible without drying any of the iron salt. The solution is then mixed with about twice its volume of water, and the silica filtered off. The first drying and heating (without hydrochloric acid) ensures the complete precipitation of the phosphorus by ammonium molybdate; whilst the second (with hydrochloric acid) facilitates the subsequent separation of the silica.

Other methods which give more or less low results have also been investigated; such are, briefly: dissolving the iron in nitric acid, evaporating to dryness, redissolving in a mixture of hydrochloric and nitric acids diluted with water, &c., which gives the same low results as dissolving in nitric acid and evaporating the solution to only half its volume: dissolve in nitric acid, boil until the solution thickens, add hydrochloric acid, boil to dryness, heat for one hour at 200°, redissolve in hydrochloric acid, &c.; the results in this case are moderately good: dissolving in aqua regia, or adding hydrochloric acid immediately after nitric acid without previous boiling; in another method the solution was prepared in a manner similar to that preceding the last, without, however, evaporating to dryness with hydrochloric acid. In all these methods the low results are of course due to the phosphorus being only partially precipitated: this is attributed to the presence of organic matter, which is, without doubt, entirely destroyed by the treatment in the first method.

The author then proceeds to give a detailed account of his method of precipitation with ammonium molybdate: the following are noteworthy. To prevent the precipitate sticking to the glass, the clean beaker employed for receiving the filtrate from the silica should simply be rinsed with water and dilute ammonia, but not wiped. The solution should be kept as small as possible. When the quantity of phosphorus exceeds several tenths of 1 per cent., 2 c.c. of molybdate solution are added in excess for every 0.001 gram of phosphorus taken. After the addition of the molybdate, the solution is kept at 40° for four hours, when precipitation is found to be complete. The washing is performed with water containing 1 per cent. of 1.20 nitric acid, and is conducted as quickly as possible. Extra washing does not tend to dissolve the precipitate. The precipitate is dried at 120°, and then contains 1.64 per cent. phosphorus. In the absence of arsenic, the method can be further accelerated, for the molybdate solution may

be added warm (50°) to the boiling iron solution, and after an hour filtered. It is proved experimentally that the addition of ammonium nitrate is not necessary when precipitating with molybdate; moreover, neither ammonium nitrate nor molybdate is required for washing the molybdenum precipitate. With regard to other methods of analysis, the "acetate magnesia" and the "molybdate magnesia" methods are referred to. The former is too tedious for general purposes, but is good as a check in doubtful cases by the molybdenum method. The molybdate magnesia method is useful when there are large amounts of phosphorus to be determined, as a large molybdenum precipitate is difficult to dry and weigh. As a general method, the ammonium molybdenum is the most convenient and practical.

It is remarked that the phosphorus in iron is not so uniformly distributed as is generally supposed. For example, in cast-iron made from the same material, the phosphorus varies from 0.020 to 0.027 per cent., or from 0.024 to 0.030 per cent. Moreover, the amount of phosphorus in bar-iron varies not only in the separate bars, but also in the different parts of the same bar. In Bessemer iron and steel ingots, it is usual to find the full amount of phosphorus of the pig-iron employed. Lancashire hearth-iron, when special care is taken, contains  $\frac{2}{3}$  or  $\frac{3}{4}$  of the phosphorus of the cast-iron, under other circumstances the amount of phosphorus varies from  $\frac{2}{3}$  to the whole, or in some few cases to more than that of the cast-iron; the phosphorus in such cases coming from the slag. Walloon hearth-iron on the other hand generally contains at the most  $\frac{2}{3}$  down to the smallest trace of the cast-iron phosphorus.

*Estimation of Phosphorus in Iron Ores.*—The most certain way to determine the total phosphorus present is to fuse with sodium carbonate, using 2 grams of carbonate to 1 gram of ore, dissolve in aqua regia, separate silica in the usual way, and proceed as above described. The ore may be efficiently dissolved in strong hydrochloric acid, taking care to digest sufficiently long before evaporation for silica, then as in the preceding case.

D. A. L.

**Detection of Adulteration in Portland Cement.** By R. and W. FRESSENIUS (*Zeitschr. Anal. Chem.*, 1884, 175—185).—Portland cement is stated to be liable to adulteration with hydraulic lime, and with furnace slag. The following tests furnish ready means of distinction between the pure article and substitutes or mixtures.

The sp. gr. of cement lies between 3.12 and 3.15, that of hydraulic lime is 2.44—2.55, and of slag 2.87—3.01. Whilst pure cement, even after lengthy exposure to the air, shows at most 2.6 per cent. of loss on ignition, lime loses from 18 to 19 per cent.: 0.5 gram of the finely powdered substance heated with 50 c.c. of cold distilled water, yields a solution which in the case of slag is practically devoid of alkalinity, whilst the lime solution requires about 20 c.c. standard acid for neutralisation, that from cement requiring from 4 to 6.2 c.c. Treated directly with standard acid, 1 gram of the substance should not consume materially less than 18.8 c.c. of acid, slag neutralising but about one-half that volume. Boiled with dilute sulphuric acid, 1 gram of the substance yields a solution which will decolorise only a few drops normal permanganate solution in the case of cement and

lime, but large volumes in that of slag. Lastly, whilst hydraulic lime absorbs carbonic anhydride (1 gram about 10 mgrms.), cement does not combine with that gas.

Experiments made with mixtures containing 10 per cent. of adulterant, readily gave decisive indications with one or other of the above tests.

O. H.

**Petroleum Testing in Tropical Climates with Abel's Apparatus.** By Sir F. A. ABEL and B. REDWOOD\* (*Chem. News*, 49, 196—197).—When the legally recognised testing method is employed, the flashing point of one and the same sample of petroleum is found to be lower in tropical than in temperate climates (compare Abel, *Jour. Soc. Chem. Ind.*, 1882, 471—478). As an illustration of this fact, the flashing point of an oil which was 73° F. in the laboratory atmosphere, was only 66° F. in an apartment heated to a tropical temperature.

This difference is due to the fact that the petroleum, having been exposed to the high temperature previous to testing, cannot so easily hold in solution the more volatile hydrocarbons, and therefore the slightest agitation—such for instance as the pouring of the oil into the testing cup—determines their vaporisation, and the volatile inflammable vapours hover about the surface of the oil in the cup and give rise to the low flashing point. This is especially the case when the oil is poured into the cup in a long thin stream from some distance above the cup. This difficulty can be obviated by prolonged cooling of the oil previous to testing; this method is, however, not recommended as practical; therefore the following are suggested:—Leaving the testing slide withdrawn for some time before applying the test-flame; removal of the vapours by aspirating, or by gently blowing over the surface; to commence applying the test-flame at a temperature much lower than that prescribed by the Acts. Of all these methods, the authors prefer the last mentioned; it causes the removal of the superincumbent vapours in quantities too small to flash by currents of air set up by each application of the test-flame. All the methods occasion the loss of some of the volatile constituents of the petroleum; as, however, there is always an unavoidable loss of these matters whenever the oils are manipulated in any way in hot climates, this loss is unimportant when compared with benefit derived from the attainment of uniform results.

D. A. L.

**Estimation of Glycerol in Aqueous Solution by means of its Refractive Power.** By F. STROHMER (*Monatsh. Chem.*, 5, 55—62).—The author recommends the estimation of glycerol in aqueous solution by a determination of the refractive index of the liquid. This can be readily and accurately effected by means of Abbé's refractometer. Tables are given showing the specific gravities and refractive indices of aqueous solutions containing from 50—99 per cent. of glycerol.

A. J. G.

\* Note by Editor.—The name is misspelt in the original.

*Note.*—The author appears to be unacquainted with Lenz's paper on this subject (*Zeitschr. Anal. Chem.*, 1880, 297).—A. J. G.

**Action of Alkalis on Amides.** By E. BOSSHARD (*Zeitschr. Anal. Chem.*, 1884, 160—165).—Contradictory statements have been made in reference to the stability of leucine, tyrosine, aspartic, and glutamic acids when heated with potassium or barium hydroxide. Thus while Mallet and also Schulze assert that ammonia is readily given off at temperatures above 50°, Schützenberger obtained amidic products by heating albumin with excess of barium hydroxide at 200° for several days.

The author prepared the amides above enumerated in a state of purity, and especially perfectly free from ammonia. These on treatment with potassium or barium hydroxide failed to yield any ammonia. Asparagine gives one-half of its nitrogen as ammonia at first, and the remainder gradually when the potash has reached a high degree of concentration.

O. H.

**Analysis of Mustard.** By A. R. LEEDS and E. EVERHART (*Bied. Centr.*, 1884, 140).—The sinapine thiocyanate or potassium myronate is estimated by treatment with aqueous alcohol, after the oil has been removed by dry ether. The solution is evaporated, dried at 105°, weighed and ignited, and the myronate is calculated from the potassium sulphate left. Myrosin and cellulose are not dissolved by dilute alcohol; these are then treated with a half per cent. soda solution; the undissolved cellulose is weighed and ignited, whilst the solution of myrosin is neutralised and precipitated by Ritthausen's solution of copper sulphate. If starch is present as an adulterant, it is converted into glucose.

E. W. P.

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### Technical Chemistry.

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**Solvent Action of Water on Zinc, and Effects of Drinking Water contaminated with Zinc.** By T. STEVENSON (*Chem. News*, **49**, 107).—Several authorities are quoted who differ in opinion as to the nocuous or innocuous effects of drinking water containing zinc. It is shown that water after passing over zinc or a zinced surface generally contains zinc in solution, or in suspension, or both. Potassium ferrocyanide is recommended as a very delicate test for zinc, but not confirmatory. D. A. L.

**Antiseptic Experiments in a Mortuary Vault.** By C. A. CAMERON (*Chem. News*, **49**, 215—216).—In the vaults of the ancient church of St. Michan, Dublin, the corpses instead of decomposing became dry, like mummies. The vaults are built of limestone. The author attributed this peculiarity in part to the dryness and freedom from dust which characterises the atmosphere of the vaults. In

order to test these antiseptic properties, several tubes of infusion of melon were prepared, sterilised, and sealed up. Many of these were opened at various times in the laboratory and speedily became turbid, &c. Ten of twelve were next carefully opened in one of the vaults which was locked for six weeks, after which period they were removed (on 13th of August, 1879); five of the tubes were filled with mycelium, the other seven were quite clear, &c. (including the sealed tubes), but after a few days' exposure to the air of the laboratory became so thick that they could not be poured out. D. A. L.

**Liquid Hydrocarbons from Compressed Petroleum Gas.** By G. WILLIAMS (*Chem. News*, 49, 197).—When the gas obtained from petroleum at a high temperature is stored under pressure, as in Pintsch's system, a liquid condenses which contains benzene, toluene, and certain olefines. In the present case, the olefines are separated from the aromatic hydrocarbons in the following manner:—The hydrocarbon vapours are passed through a powerful rectifying column, and two fractions are collected, one below and the other above 66°. The first is reserved for the preparation of the olefines: the latter is used for the preparation of benzene, &c., for which purpose the olefines are removed by agitation with cold permanganate solution, or preferably by distillation from dilute nitric acid; the latter method is susceptible of yielding accurate quantitative results. Nitro-products obtained in the latter process are under examination.

D. A. L.

**Paraffin-shale from Servia.** By A. B. GRIFFITHS (*Chem. News*, 49, 137—138).—This shale, intermingled with beds of whitish clay containing rock-salt and sodium and magnesium sulphides, forms a very extensive deposit near the River Golabara in Western Servia. It is nearly white and odourless, and contains no bituminous matter. When heated to about 426° it takes fire and burns with a clear, bright, smokeless flame, leaving a grey ash. On distillation, it yields 2 per cent. of a semi-solid hydrocarbon, of which 1.75 per cent. is wax soluble in petroleum. In addition to this, it contains 3.02 per cent. of water and 1.18 per cent. of ammonia, the remainder being mineral matter, which would probably be useful for the preparation of a hydraulic cement.

D. A. L.

**Presence of Manganese in Wines and other Vegetable and Animal Products.** By E. J. MAUMENÉ (*Compt. rend.*, 98, 1056—1058).—Thirty-one wines of different vintages from various localities in Europe and Africa were found to contain amounts of manganese varying from 0.0001 to 0.0020 gram per litre. All these wines contained an extremely minute proportion of potassium hydrogen tartrate, but in other respects were of normal composition. Wheat grown in the district of Beaujolais contains a considerable proportion of manganese, and this metal is also present in many other vegetable and animal organisms, details concerning which will be given in subsequent papers.

C. H. B.

**Preserving Ground Coffee.** By F. SCHNITZER (*Dingl. polyt. J.*, **250**, 554).—Ground coffee is mixed with a certain proportion of calcium sucate, with or without the addition of pure powdered sugar, and the mixture pressed into cakes. The calcium sucate is said to prevent decomposition, *i.e.*, it fixes the organic acids formed at the commencement of the decomposition. D. B.

**Manufacture of Etching Ink.** (*Dingl. polyt. J.*, **250**, 555).—According to Müller, a liquid for etching on glass has recently been introduced into commerce, and can be used with an ordinary pen. It consists of hydrofluoric acid, ammonium fluoride, and oxalic acid, and is thickened with barium sulphate. A better ink is obtained as follows:—Equal parts of the double fluoride of hydrogen and ammonium and dried precipitated barium sulphate are ground together in a porcelain mortar. The mixture is then treated in a platinum, lead, or gutta-percha dish with fuming hydrofluoric acid, until the latter ceases to react. D. B.

**Process for Preserving and Colouring Stone Work.** By A. KEIM and J. THENN (*Dingl. polyt. J.*, **250**, 556).—The authors preserve white stones without changing their original colour by drenching them with lime, baryta-water, magnesium sulphate, or potash alum, then with potash water-glass, and finally with hydrofluosilicic acid. If it is intended to colour the stone work, metallic sulphates are used, the bases becoming fixed by the potash water-glass, and the sulphuric acid combining with the baryta, whilst the potash unites with the hydrofluosilicic acid. The stones are then painted with a solution of paraffin in benzene or petroleum. D. B.

**The Liebig Memorial Statue at Munich.** By M. v. PETTENKOFER, A. BAEYER, and C. ZIMMERMANN (*Ber.*, **17**, 230—234).—On November 6th, 1883, it was found that the marble statue of Liebig was covered with a number of black spots and stripes. Further examination showed these stains to consist of a mixture of silver and a little hydrated manganese dioxide. From this it is very probable that the liquid employed to deface the statue was a solution of silver nitrate and potassium permanganate. The method employed for the removal of the stains was founded on the conversion of the metals into sulphides and subsequent solution of the sulphides by means of potassium cyanide. Each stain was covered with a paste made of yellow ammonium sulphide and porcelain clay. This was renewed after 24 hours, and after the lapse of another day carefully washed off, and each stain then treated twice in succession with a paste of porcelain clay and concentrated solution of potassium cyanide. In most cases this was sufficient to remove all stain, but some few of the very deep stripes had to be treated in this way several times to effect complete removal. The success of the operation was so complete, that no sign of the stains can be seen now. A. J. G.

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## General and Physical Chemistry.

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**Skrivanoff's Cell (Pocket Form).** By D. MONNIER (*Compt. rend.*, 98, 224).—This cell is formed of plates of zinc and of chloride of silver wrapped in parchment-paper and immersed in a concentrated solution of potassium hydroxide, contained in a gutta-percha vessel, which may be hermetically sealed. The external conductors are of silver, and the cell complete weighs about 100 grams. Its electromotive force is 1.5 volt, and it will maintain a current of 1 ampère for an hour, when it becomes necessary to renew the alkaline solution. R. R.

**Variation of Electromotive Force in Accumulators.** By E. REYNIER (*Compt. rend.*, 98, 224—225).—The secondary electromotive force is decidedly greater during the charge of accumulators than during the discharge. Of the three kinds of accumulator examined, the difference was found to be greatest in that formed with copper, lead peroxide, and acidulated solution of copper sulphate; much less in Planté's accumulator; and least in that made with amalgamated zinc, lead peroxide, and acidulated zinc sulphate solution. R. R.

**A Mercurial Galvanometer.** By G. LIPPMANN (*Compt. rend.*, 98, 1256—1257).—A mercurial manometer with a narrow tube is placed between the arms of a fixed magnet in such a way that the horizontal branch of the manometer passes between the poles of the magnet. The current to be measured passes vertically through the horizontal limb of the manometer, and produces a difference in level in the two branches of the manometer, which is proportional to the intensity of the current. That portion of the column of mercury through which the current passes, constitutes a moveable conductor which tends to repel the magnet in its neighbourhood. Since, however, the magnet is fixed, the conductor itself is displaced, and produces hydrostatic pressure resulting in an alteration of the levels of the mercury. The sensibility of the galvanometer increases with the intensity of the magnetic field, and with a decrease in the diameter of the column of mercury through which the current passes.

This apparatus is reversible; if the mercury is moved mechanically, an electric current is produced in the circuit forming the poles of the apparatus. C. H. B.

**Joule's Law.** By P. GARBE (*Compt. rend.*, 98, 360—363).—The paper describes the electrometric measurement of energy radiated from incandescent lamps, and the results are found to be in complete accordance with Joule's law. R. R.

**Electric Conductivity of very Dilute Saline Solutions.** By E. BOUTY (*Compt. rend.*, 98, 140—142).—The experiments recorded



in this paper tend to prove that the more dilute the saline solutions operated on, the more closely do their relative electric resistances approximate to the ratios between the "equivalents" of the respective salts compared.

The author believes that dilution tends to eliminate the differences due to interfering causes, such as non-identity of the physical properties of the solution, and formation of more or less stable hydrates, &c., and that in the limit the conductivity of solutions containing in the same volume quantities of neutral salts proportional to their "equivalents," is the same, that is, the molecular conductivity of all the neutral salts is the same.

R. R.

*Note by Abstractor.*—By "equivalents" is here meant the sum of the "equivalent" weights in the formula of the salt,  $O = 8$ .—R. R.

**Faraday's Law, and the Law discovered by Bouty.** By WURTZ (*Compt. rend.*, 89, 176).—Bouty thinks that the expression (see preceding Abstract) of these laws in terms of the *atomic* weights, is obscure and complicated. Now for 1 atom of chlorine liberated at the positive pole, the quantities of metal deposited at the negative pole in the electrolysis of the chlorides  $\text{NaCl}$ ,  $\text{Cu}_2\text{Cl}_2$ ,  $\text{CuCl}_2$ ,  $\text{BiCl}_3$ ,  $\text{SnCl}_4$ ,  $\text{Fe}_2\text{Cl}_6$  are  $\text{Na}$ ,  $\frac{2\text{Cu}}{2}$ ,  $\frac{\text{Cu}}{2}$ ,  $\frac{\text{Bi}}{3}$ ,  $\frac{\text{Sn}}{4}$ ,  $\frac{2\text{Fe}}{6}$ , and these quantities are strictly equivalent, although they by no means correspond to the "equivalents" in the case of cuprous, bismuthic, stannic and ferric chlorides. Similarly, in the electrolysis of  $\text{HCl}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_3\text{N}$ , for one volume of hydrogen liberated at the negative pole, there is set free at the positive pole 1 vol. chlorine,  $\frac{1}{2}$  vol. oxygen,  $\frac{1}{3}$  vol. nitrogen. These last are strictly equivalent, but it cannot be said that  $\frac{1}{3}$  vol. nitrogen represents 1 equivalent of nitrogen. But here it is a question neither of atomic weights, nor of "equivalents" in the sense usually attached to that word, but in fact of the valency or atomicity of the elements, a notion that has superseded the old idea of equivalents.

Bouty has shown that the electric resistance of saline solutions is the same when they contain equivalent quantities of metal. But as the above-mentioned chlorides do not contain equivalent quantities of metal, there is reason to believe that the *molecules*, which differ so much by their form and relative sizes, will oppose different *molecular* resistances to the current.

R. R.

**Electric Conductivity of very Dilute Saline Solutions.** By E. BOUTY (*Compt. rend.*, 89, 362—365).—The electric conductivity of a neutral salt in a very dilute solution increases with the temperature, thus:— $C_t = C_0(1 + kt)$ . The value of  $k$  is the same for all neutral salts, and is equal to 0.033543.

R. R.

**Electric Conductivity of Saline Solutions.** By WURTZ (*Compt. rend.*, 98, 176).—Referring to the paper of Bouty (preceding Abstract), the author remarks that Bouty has shown that the electric resistance of saline solutions is the same when the solutions contain

equivalent quantities of metal. Otherwise he thinks the molecules must offer different resistances to the electric current on account of the difference of their forms and sizes, and therefore he would not expect to find the same conductivity in such salts as  $\text{NaNO}_3$ ,  $\text{NaSO}_4$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{Na}_4\text{P}_2\text{O}_7$ . R. R.

**Temperature Regulator.** By L. MEYER (*Ber.*, **17**, 478—484).—In order to maintain an air-bath at a constant temperature, the author recommends the use of a modification of Babo's gas regulator. The apparatus cannot be intelligibly described without the accompanying woodcut. The "rheometers" of Giroud of Paris are also very useful when one and the same temperature is always required. Each rheometer allows a definite number of litres of gas (*e.g.*, 50, 60, 80, 100 up to 200 litres) to pass through it per hour. W. C. W.

**Law of Thermic Substitution Constants.** By D. TOMMASI (*Compt. rend.*, **98**, 368).—The author contends that his law of thermic constants is applicable to all soluble salts without exception, and that dissociation explains those cases in which the law appears to fail. R. R.

**Bromine Substitution.** By BERTHELOT and WERNER (*Compt. rend.*, **98**, 1213—1218).—It is usually very difficult to determine the thermal disturbance accompanying substitution, because in most cases the reactions proceed very slowly at ordinary temperatures, and secondary products are frequently formed. The action of bromine on the phenols, however, takes place rapidly, and yields a definite product. The heat of formation of tribromophenol was determined by the action of bromine, both pure and in aqueous solution, on an aqueous solution of phenol; by the action of bromine on phenol in presence of potassium bromide; and by the action of bromine on sodium phenolate. The heat of formation of dibromophenol was determined by the action of bromine on sodium dibromophenolate, and that of the monobromo-derivative by the action of the proper proportion of bromine on sodium phenolate, and by the action of bromine on monobromophenol. The mean results obtained were—

$\text{C}_6\text{H}_5\text{O}$ diss. + $\text{Br}_2$ diss. = $\text{C}_6\text{H}_5\text{BrO}$ solid +	
HBr diss. ....	develops + 26.1 cal.
$\text{C}_6\text{H}_5\text{O}$ diss. + $2\text{Br}_2$ diss. = $\text{C}_6\text{H}_4\text{Br}_2\text{O}$ solid +	
$2\text{HBr}$ diss. ....	„ + 46.0 „
$\text{C}_6\text{H}_5\text{O}$ diss. + $3\text{Br}_2$ diss. = $\text{C}_6\text{H}_3\text{Br}_3\text{O}$ solid +	
$3\text{HBr}$ diss. ....	„ + 68.3 „
or—	
$\text{C}_6\text{H}_5\text{O}$ solid + $\text{Br}_2$ gas = $\text{C}_6\text{H}_5\text{BrO}$ solid +	
HBr gas ....	„ + 12.1 „
$\text{C}_6\text{H}_5\text{O}$ solid + $2\text{Br}_2$ gas = $\text{C}_6\text{H}_4\text{Br}_2\text{O}$ solid +	
$2\text{HBr}$ gas. ....	„ + 20.4 „
$\text{C}_6\text{H}_5\text{O}$ solid + $3\text{Br}_2$ gas = $\text{C}_6\text{H}_3\text{Br}_3\text{O}$ solid +	
$3\text{HBr}$ gas. ....	„ + 31.0 „
	3 0 2

The amount of heat developed is approximately proportional to the amount of bromine introduced, and is about + 10·5 cal. for each atom of bromine. The introduction of a fourth atom of bromine, however, develops a much smaller quantity of heat, a result which agrees with the known stability of the tribromo-derivative. The number + 10·5 cal. is approximately one-third the heat of formation of hydrobromic acid from its elements (27 cal.); hence it follows that the simple substitution of bromine for hydrogen would absorb  $3 \times 3$  cal., which indicates that substitution in the phenols only takes place by reason of the heat developed by the simultaneous formation of hydrobromic acid.

C. H. B.

**Thermochemistry of the Oxychlorides of Mercury.** By G. ANDRÉ (*Compt. rend.*, **98**, 298—300).—From experiments described in the paper, the quantities of heat disengaged in the following combinations are deduced :—

$\text{HgO} + \text{HgCl}_2$	.....	+ 3·30 cal.	
$2\text{HgO} + \text{HgCl}_2$	.....	+ 6·30	„
$3\text{HgO} + \text{HgCl}_2$	.....	+ 7·90	„
$4\text{HgO} + \text{HgCl}_2$	.....	+ 9·86	„

R. R.

**Thermochemistry of Antimony Fluoride.** By GUNTZ (*Compt. rend.*, **98**, 300—303).—Hydrofluoric acid, even when very dilute, rapidly dissolves crystallised or amorphous antimony oxide, and the solution, unlike that of other antimony salts, is not decomposed by water; on evaporation over the water-bath, it leaves crystallised antimony fluoride. As antimony fluoride dissolves in hydrofluoric acid with liberation of heat, which increases with the quantity of acid until eight molecular weights of the latter are present for one of the fluoride, there is reason to believe that an acid fluoride is formed. The author has not succeeded in isolating this compound in a pure state, although he has obtained a crystallised fluoride containing an excess of acid. The thermic determinations of the formation of antimony fluoride and oxide perfectly explain the stability of the former in presence of water, and furnish another experimental confirmation of the theory advanced by Berthelot in his *Mécanique chimique*.

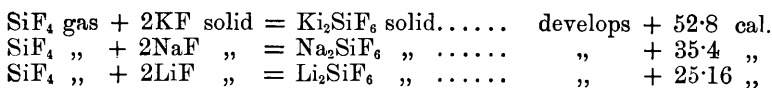
R. R.

**Thermochemistry of Alkaline Fluosilicates.** By C. TRUCHOT (*Compt. rend.*, **98**, 1330—1333).—The heats of formation of potassium, sodium, and lithium silicofluorides were determined by three different methods.

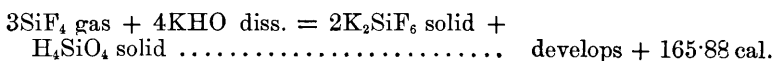
(1.) *Action of Silicon Fluoride on the Alkaline Fluorides*—

$\text{SiF}_4$ gas	+ 2KF diss.	= $\text{K}_2\text{SiF}_6$ solid	.....	develops	+ 45·6 cal.
$\text{SiF}_4$ „	+ 2NaF „	= $\text{Na}_2\text{SiF}_6$ „	.....	„	+ 36·6 „
$\text{SiF}_4$ „	+ 2LiF solid	= $\text{Li}_2\text{SiF}_6$ diss.	.....	„	+ 27·0 „

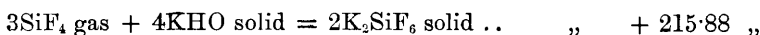
Potassium and sodium silicofluorides are insoluble in solutions of the corresponding fluorides, which were always in excess. The heat of solution of lithium silicofluoride = + 1·84 cal., hence—



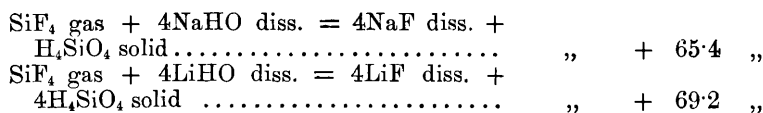
(2.) *Action of Silicon Fluorides on Dilute Solutions of the Hydroxides.*—This reaction yields a fluosilicate in the case of potassium only; in the other two cases a simple fluoride is formed—



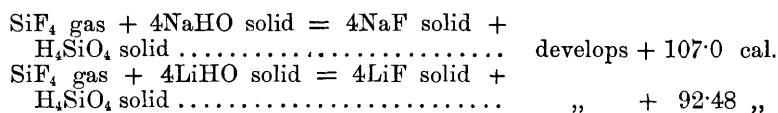
hence—



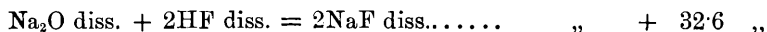
In the other two cases—



The silicic acid liberated in these reactions is not acted on by potash, and the action of lithia is negligible; but the action of soda varies with the proportion in which it is present in excess. A correction being made for this secondary action, it is found that—

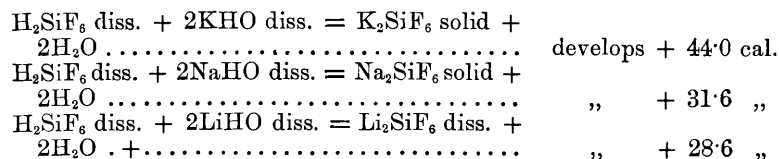


Thomsen has found that—

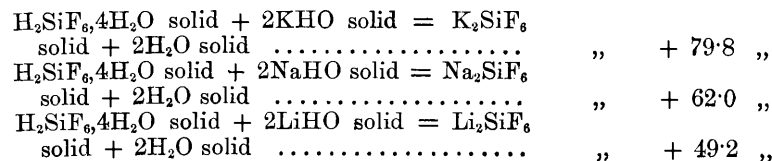


hence it follows that if H is substituted for Na in one of the above reactions, we find that  $\text{SiF}_4 + 4\text{H}_2\text{O} + n\text{H}_2\text{O} = 4\text{HF}$  dil. +  $\text{H}_4\text{SiO}_4$ , develops practically 0 cal., a result which explains why the action of silicon fluoride on water does not take place in this manner.

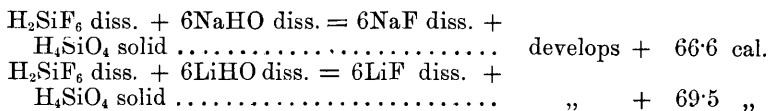
(3.) *Action of Fluosilicic Acid on Dilute Alkalis*—



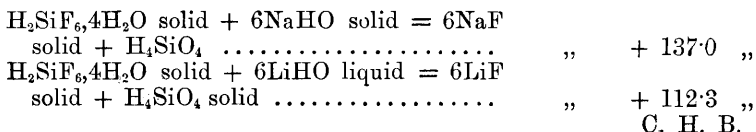
whence—



If 6 mols. of sodium or lithium hydroxide are allowed to act on 1 mol. of fluosilicic acid, the reaction is entirely different—



whence—



**Determination of Vapour-densities by Gaseous Displacement under Low and Variable Pressures.** By J. MEUNIER (*Compt. rend.*, **98**, 1268—1271).—The apparatus employed is a modification of that of Crafts and Meyer (*Bull. Soc. Chim.*, **33**, 550). The upper part of each limb of the graduated U-tube is provided with a stopcock so that they communicate with each other and with a vacuum globe. Above the stopcock, on the left branch of the tube, is sealed a capillary tube which communicates with the heated reservoir. By this arrangement, communication between the reservoir and left limb of the tube, and the vacuum globe, can be cut off or opened as required. The two branches of the tube are graduated in millimetres and filled with strong sulphuric acid, the tube being surrounded by cold water. The reservoir is heated by means of some liquid boiling at the required temperature, and communication is opened between the apparatus and the vacuum vessel. The communication between this vessel and the left limb of the tube is then cut off. If the levels of the sulphuric acid in the U-tube remain stationary, indicating that the temperature is constant, the pressure in the vacuum vessel  $h$ , the temperature of the water surrounding the U-tube  $t$ , and the levels of the sulphuric acid in each limb of the tube are read off, and the substance is dropped into the reservoir. When the evolution of gas ceases, the levels of the sulphuric acid are again read off, and the density is calculated by means of the formula

$$D = \frac{P + 76 \times (1 + \alpha t)}{1.293 \times v h},$$

where  $P$  is the weight of the substance taken. In this formula,  $v$  represents the volume of air expelled at the pressure  $h$ , but the volume  $v'$  actually read off is smaller, because the pressure has changed to  $h'$  in consequence of the alteration in the levels of the sulphuric acid. The true value of  $vh$  is obtained with sufficient accuracy by means of the expression  $vh = V(h' - h) + v'h'$ .

If the levels of the sulphuric acid are made equal, so that  $h = h'$ , the formula becomes identical with Victor Meyer's. The volumes corresponding with the divisions on the left branch of the U-tube are determined by calibration with mercury, and the volume  $V$  of the reservoir, connecting tube, and left limb of the U-tube down

to the initial graduation, are determined by Regnault's manometric method.

This method gives accurate results even at low pressures. An amount of the substance should be taken sufficient to cause a difference of 0.15 metre between the levels of the sulphuric acid. When too large a quantity of the substance is taken, the expulsion of gas ceases, and the sulphuric acid acquires a constant level when the vapour attains the maximum tension corresponding with the temperature of the reservoir, this tension being measured by  $h$ . By operating in this way at various temperatures, it will be possible, with very small quantities of matter, to ascertain the curves representing the vapour-tension, and thus determine the boiling point of substances which boil with decomposition at high temperatures.

Determinations of the vapour-density of the new isomeride of benzene hexachloride (this vol., p. 733) by the above method gave 9.186, which shows that its formula is  $C_6H_6Cl_6$ . C. H. B.

**Differential Dilatometer and its Application in an Investigation on the Formation of Alums.** By W. SPRING (*Ber.*, **17**, 404—408).—E. Wiedemann (*Ann. Phys. Chem.*, **17**, 561) has recently pointed out that the alums and other salts containing water of crystallisation, lose a portion of their water and are converted into salts of different composition by an increase in temperature. This fact explains why the author obtained constant results in his experiments on the dilatation of alums (*Ber.*, **15**, 1254), when the salts had been previously heated at 70°, and varying results when this had not been done.

By means of a dilatometer (the construction of which cannot be described without the accompanying woodcut), the author has measured the relative contraction which takes place, owing to dissociation, when the different alums are heated from 0° to 70°. Thallium, potassium, and chromium alums all contract more than ammonium alum. W. C. W.

**Solubility of Salts.** By ÉTARD (*Compt. rend.*, **98**, 1276—1279).—The author has previously shown (this vol., 807) that the solubility of all salts is proportional to the temperature, and is therefore represented by a straight line. Any deviations from this law are merely temporary, and correspond with the dissociation of the combination between the dissolved substance and the solvent. The curves representing the solubilities of various salts as determined by other observers are generally straight lines, and in cases where the curve is inflected, the determinations have been made between too narrow limits of temperature. When the determinations are extended to higher and lower temperatures, it is found that the solubility follows the law already stated. In order to describe concisely the solubility of a salt, it is sufficient to express the straight portions of the curve of complete solubility by the formula  $s = a + bt$ , and to give some points on the curve of deviation. The curves representing the solubility of the haloid salts of a family of metals such as Ca, Ba, Sr, or Mg, Zn, Cd, are almost identical.

For determinations of solubility at low temperatures, methyl chloride may be used with advantage, and will give a temperature of  $-20^{\circ}$ . To determine solubilities at high temperatures, an excess of the crystallised salt is introduced, together with a certain quantity of the cold saturated solution, into a strong glass tube. The tube is drawn out in the middle to about half its original diameter, bent at the contraction at an angle of  $45^{\circ}$ , and the open end sealed. It is then heated at the required temperature, with occasional agitation, and after a sufficient length of time the tube is inverted so as to decant the saturated solution from the first limb into the second. Matters are so arranged that the two limbs of the tube are of equal capacity, and both contain the same quantity of liquid (about 15 grams). In this way, errors due to unequal condensation of the vapour are avoided. When the tube has cooled to about  $90^{\circ}$  it is cut at the bend, the second half and its contents weighed, the contents analysed, and the empty tube weighed afterwards. Concordant and accurate results are obtained, and the curve representing these results is a continuation of that representing the results under ordinary pressure. It is evident therefore that the influence exerted by pressure on the solubility, within the limits of temperature employed, is very slight. Moreover, the solubility above  $100^{\circ}$  undergoes perturbations strictly analogous to those observed at lower temperatures, sometimes increasing, sometimes rapidly diminishing.

The solubility of sodium chloride between  $0^{\circ}$  and  $100^{\circ}$  is represented by the formula  $S = 26.4 + 0.0248t$ , if 26.4 is the amount dissolved at  $0^{\circ}$ ; and the author finds that this formula holds good up to  $160^{\circ}$ . When, however, the solubility is determined at low temperatures, it is found that below  $0^{\circ}$  the curve of solubility alters, and at  $-21^{\circ}$  the solution contains only 23.5 per cent. of salt, instead of 26.0 as required by the formula. This deviation in the curve takes place at the temperatures at which the hydrate  $\text{NaCl} \cdot 2\text{H}_2\text{O}$  is respectively formed and dissociated, and thus agrees with the author's theory.

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C. H. B.

## Inorganic Chemistry.

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**Liquefaction of Hydrogen.** By S. WROBLEWSKI (*Compt. rend.*, **98**, 304—306).—The author compressed hydrogen gas under 100 atmospheres in a vertical tube of 0.2 mm. diameter. The apparatus was so constructed that the pressure could be removed instantaneously when the tube had been cooled by the vaporisation of liquid oxygen. The moment the pressure was removed, ebullition took place in the tube, similar to that observed by Cailletet with oxygen, in his experiments of 1882; it occurred at a certain distance from the bottom of the tube, continued but a short time, and was less marked and more difficult to observe than in the case of oxygen. The reason of this difficulty is that the density of liquid hydrogen, as deduced by



Cailletet and Hautefeuille, being only 0.033, and the density of gaseous hydrogen at low temperatures and under moderate pressure being nearly the same, the liquid and the gaseous parts are not optically distinguishable. The analogy between these phenomena and those presented by oxygen leads to the conclusion that the temperature required for the complete liquefaction of hydrogen is not far removed from that which may be obtained by the ebullition of liquid oxygen. R. R.

**Liquefaction of Hydrogen.** By R. OLSZEWSKI (*Compt. rend.*, 98, 365).—Referring to Wroblewski's paper (preceding Abstract) the author states that he was unable to liquefy hydrogen by submitting it to a pressure of 100 atmospheres, cooling with liquid oxygen, and sudden removal of pressure. Nor did he succeed when liquefied air, boiling in a vacuum, was substituted for the oxygen. More recently he has liquefied hydrogen under a pressure of 190 atmospheres, cooling with oxygen boiling in a vacuum. When the pressure is suddenly removed, a momentary ebullition takes place, and small colourless drops are projected into the upper part of the tube. R. R.

**Expansion of Elementary Gases.** By J. M. CRAFTS (*Compt. rend.*, 98, 1259—1261).—A criticism of Berthelot's paper on this subject. Chlorine gas has an abnormally high specific heat even below 200°, but it obeys the ordinary laws of expansion of gases up to 1400°, and similar phenomena are observed in the case of bromine and iodine. There is therefore no correlation between the coefficient of expansion of a gas and its specific heat. The heat which is absorbed without increasing the energy of translation of the molecules increases their internal energy, and thus facilitates their dissociation at a higher temperature. C. H. B.

**Crystallisation of Sulphur.** By D. GERNEZ (*Compt. rend.*, 98, 144—146).—When sulphur has been heated to 160°, allowed to cool to 100°, and maintained at that temperature for some time, the liquid is capable of yielding several crystalline modifications. By rubbing the interior surface of the vessel, and by other means, a deposition of pearly crystals is caused, and the liquid from which these have separated may be converted at will into the ordinary prismatic, or the octahedral crystals of sulphur by the touch of a corresponding crystal. The experiments described in the paper show that the conversion of the fused sulphur into the ordinary crystals takes place with sevenfold rapidity in the liquids from which the nacreous crystals have been deposited, as compared with the same liquid before such deposit has taken place. The author considers that at the temperature of 160° the allotropic modification that crystallises with pearly lustre is produced, and by its solution in the rest of the liquid the latter is in the condition of a supersaturated solution. R. R.

**Physical Properties of Sea-water and Ice.** By O. PETTERSSON (*Bied. Centr.*, 1884, 61—63).—The investigations were carried on during the expedition of the "Vega," in the Siberian Sea, where salt

water in all grades of saturation was found from 3·4 per cent. of solid residue in the lower strata to almost soft water at the surface from the many rivers which flow into the sea. The experiments related to the changes in temperature and volume at freezing point of pure water, brackish water with slight proportion of salt, and of sea water. Previous experiments had shown the author that the presence of foreign bodies capable of passing into solution with another substance greatly altered the melting process. The general results of the experiments justify previous opinions, and show that the process of thawing begins at a point below the freezing point; skating is unpleasant on fresh-water ice, from yielding; in Arctic seas, the ice takes deep impressions at much lower temperatures; ice from open seas is considered useless in commerce because it softens and melts at temperatures when fresh-water ice is clear and hard.

He explains the phenomenon of the dreaded heaping up of pack ice in Arctic seas, thus: a sudden fall in the temperature causes the superficies of the ice fields to extend enormously, the lower strata remaining somewhere about freezing point; a further fall of temperature causes a violent contraction and splitting up of the ice with loud noises. He answers the question as to whether sea-water ice contains salt in the affirmative, and says it is present both mechanically in the pores and chemically in the substance; but that whilst chlorides predominate in water, sulphates are chiefly found in the ice. J. F.

**Crystallised Ammonio-Silver Chloride and Ammonio-Silver Iodide.** By TERREIL (*Compt. rend.*, 98, 1279—1280).—When silver chloride saturated with ammonia is heated with a saturated solution of ammonia in a sealed tube at 100°, the chloride dissolves in large quantity, and the solution, on cooling, deposits long white lamellar prisms, formed by the aggregation of needles. They rapidly give off ammonia when exposed to the air, are blackened by light, and are decomposed by water. When dried over quick-lime, they have the composition  $\text{AgCl}, 2\text{NH}_3$ .

Silver iodide, when treated in the same way, is only slightly soluble, and yields thin white micaceous plates, which rapidly acquire a violet tint. The undissolved amorphous portion remains permanently white. If the violet plates are heated with the ammonia, they dissolve, and separate again in a colourless condition on cooling. When exposed to the air, these crystals give off ammonia, lose their violet tint, and become yellow. They have the composition  $\text{AgI}, 2\text{NH}_3$ , and are shown by microscopical examination to be octagonal tables.

Ammoniacal silver bromide was treated in the same way; but as soon as the water in the water-bath boiled, the silver bromide melted, and in a few minutes there was a very violent explosion. It would seem, therefore, that ammoniacal silver bromide is very slightly soluble in ammonia, melts at about 90°, and detonates at about 100°. Ammoniacal silver phosphate, under the same conditions, dissolves rapidly, but the liquid quickly turns brown and deposits an amorphous brownish-black substance resembling silver fulminate.

C. H. B.

**Barium Hydrogen Phosphates.** By A. JOLY (*Compt. rend.*, **98**, 1274—1276).—When monobarium hydrogen phosphate is brought in contact with a constant quantity of water in proportions varying from 1 to 72 per cent., the ratio of the total phosphoric acid to that remaining in combination increases from 1 to 1.99, or, in other words, the most concentrated solution which can be obtained by bringing an excess of monobarium hydrogen phosphate in contact with water, contains 2 equivalents of the acid to 1 equivalent of the base. One-third of the phosphoric acid is dissolved in its original state of combination, whilst the remaining two-thirds are decomposed into dibasic phosphate, which is precipitated, and free phosphoric acid, which remains in solution.

The decomposition of monobarium hydrogen phosphate by water takes place in two phases. At first, as the total weight of the salt brought in contact with the same quantity of water increases in arithmetical progression, the weight which is dissolved without decomposition decreases in geometrical progression; but as soon as about half the original salt has been decomposed, the character of the reaction changes, and a di-acid salt,  $\text{BaO}, 2\text{P}_2\text{O}_5 + x\text{H}_2\text{O}$ , is formed in the liquid. The proportion of this salt increases as the acidity of the liquid increases, and eventually it exists alone in solution.

The phenomena observed when the most acid solutions are diluted with water in presence of the precipitated dibarium phosphate, are analogous to those observed in the case of the calcium phosphates (this vol., p. 556).  
C. H. B.

**New Method for Preparing Barium Permanganate.** By G. ROUSSEAU and B. BRUNEAU (*Compt. rend.*, **98**, 229—231).—All attempts to obtain barium permanganate directly from manganic peroxide and barium salts failed; but a satisfactory method was found in the decomposition of potassium permanganate by hydrofluosilicic acid, using the latter in slight excess. The mixture is kept cool, and after the separation of the potassium fluosilicate, the clear supernatant liquor is decanted and the deposit drained on an asbestos filter and washed. The solution containing permanganic and hydrofluosilicic acids is saturated in the cold with barium hydroxide. The solution of barium permanganate, after separation of the insoluble barium fluosilicate, is evaporated until the salt crystallises out on cooling. The crystals may be obtained in very large orthorhombic octahedra, almost black, with a violet reflection.  
R. R.

**Solubility of Calcium Hydroxide in Water at Different Temperatures.** By T. MABEN (*Pharm. J. Trans.* [3], **14**, 505—506).—After referring to the numerous conflicting statements made by various eminent authorities with regard to the solubility of calcium hydroxide in water, the author proceeds to describe his method of investigating this subject and its results. Pure calcium oxide is slaked with distilled water. The slaked lime and water are left in contact in a flask in a bath, which is kept at a definite temperature. When the lime and water is of the required temperature, the mixture is filtered through a funnel kept at the same temperature. Ther-

mometers were used in the funnel as well as the flask. The results are as follows:—

Temperature.	Parts of water to dissolve 1 part CaO.	Temperature.	Parts of water to dissolve 1 part CaO.	Temperature.	Parts of water to dissolve 1 part CaO.
0°	759	35°	909	70°	1235
5	764	40	932	75	1313
10	770	45	985	80	1362
15	779	50	1019	85	1388
20	791	55	1104	90	1579
25	831	60	1136	95	1650
30	862	65	1208	99	1650

In addition to this effect of temperature, the presence of calcium carbonate also interferes with the solubility of calcium hydroxide: hence it is important when lime-water of definite strength is required, as in pharmaceutical purposes, that the lime should be kept out of contact with the air if it is to be employed for the preparation of lime-water; the latter should also be kept in a well-stoppered bottle. One part of calcium carbonate is soluble in 40,000 of water, giving it a distinctly alkaline reaction.

D. A. L.

**Molecular Calcium Compounds.** By C. W. FOLKARD (*Chem. News*, 49, 258).—By exposing calcium hydroxide to hydrogen sulphide until it ceases to gain weight, a grey powder is obtained containing hydrogen sulphide very feebly combined with calcium hydroxide in the proportions represented by the formula  $4\text{Ca}(\text{HO})_2, 3\text{H}_2\text{S}$ . Hydrogen sulphide is evolved from this substance by the action of coal-gas, and at 100° water is eliminated, leaving a compound  $2\text{CaH}_2\text{O}_2, 2\text{CaOH}_2\text{S}$ . This grey-green compound loses 1 mol.  $\text{H}_2\text{O}$  at a gentle heat, in a current of coal-gas, yielding a yellowish-white salt,  $2\text{CaH}_2\text{O}_2, \text{CaOH}_2\text{S}, \text{CaS}$ ; and this at a red heat out of contact with the air yields up 2 mols.  $\text{H}_2\text{O}$ , producing the substance  $2\text{CaO}, \text{CaOH}_2\text{S}, \text{CaS}$ , which, when ignited in the air, burns like tinder, producing calcium sulphate. (*Comp. Divers, Trans.*, 1884, p. 270.)

D. A. L.

**Preparation of Dicalcium and Tricalcium Phosphate.** By C. L. DE BOUQUET (*Dingl. polyt. J.*, 252, 88).—The author employs calcium hydrogen sulphide for the precipitation of acid solutions of phosphates.

D. B.

**Expansion of Alums.** By W. SPRING (*Ber.*, 17, 408—412).—The following numbers show the expansion of alums which have been previously heated at 60—70° in a vacuum, and of alums which have not been heated.

*Alums not previously Heated.*

°.	Ammonium aluminium.	Potassium aluminium.	Rubidium aluminium.	Cæsium aluminium.	Thallium aluminium.	Potassium chromium.
0	1·000000	1·000000	1·000000	1·000000	1·000000	1·000000
20	1·000136	1·000148	1·000063	1·000097	1·000267	1·001008
40	1·000275	1·000299	1·000442	1·000945	1·000551	1·002039
50	1·000652	1·000475	1·001118	1·002577	1·001883	1·003092

*Alums previously Heated at 70° in vacuo.*

20	1·00096	1·001013	1·000897		1·001086	1·000961
40	1·00162	1·002076	1·00170		1·001779	1·001898
50	1·00163	1·002602	1·001981		1·001925	1·002348

*Specific Gravities of Alums Dried at Ordinary Temperature.*

0	1·6413	1·753	1·8852	1·9852	2·3256	1·8308
50	1·6401	1·7523	1·8830	1·980	2·3212	1·8259

*The same Dried at 70°.*

0	1·6427	1·7602	1·8705		2·3226	1·8293
50	0·640	1·7556	1·8668		2·3181	1·8250

W. C. W.

**Action of Potassium Sulphide on Mercuric Sulphide.** By A. DITTÉ (*Compt. rend.*, 98, 1271—1273).—When mercuric sulphide is brought in contact with a dilute solution of potassium sulphide, a certain quantity of the former is simply dissolved, but no other change takes place even if the substances are left in contact for several months. If, however, the alkaline solution is moderately concentrated, the excess of mercuric sulphide is converted into brilliant black needles of the composition  $5\text{HgS}, \text{K}_2\text{S}$ , the change being more rapid the higher the temperature. The crystals are larger and more brilliant the more slowly they are formed. They are decomposed by water, which gradually removes the alkaline sulphide and leaves a residue of mercuric sulphide, the decomposition taking place much more rapidly on heating.

If the solution of potassium sulphide is very highly concentrated, a large quantity of mercuric sulphide is dissolved, and the excess is gradually converted in the cold into brilliant transparent white needles of the composition  $\text{HgS}, \text{K}_2\text{S}, 7\text{H}_2\text{O}$ . If the liquid is heated, the excess of the sulphide is converted, not into white needles, but into brilliant golden-yellow plates, of the composition  $\text{HgS}, \text{K}_2\text{S}, \text{H}_2\text{O}$ . The formation of this double sulphide develops a considerable amount of heat. When powdered mercuric sulphide is allowed to fall into a cold concentrated solution of potassium sulphide, it instantly forms a hard compact mass, the liquid becomes very hot, and after some time the mercuric sulphide is completely converted into white crystals.

The sulphide  $\text{HgS}, \text{K}_2\text{S}$  dissolves without decomposition in a cold concentrated solution of potassium sulphide, but is decomposed by a

dilute solution or by pure water. If the concentrated solution is gradually heated, the liquid becomes turbid at a certain temperature and the sulphide  $5\text{HgS}, \text{K}_2\text{S}, 5\text{H}_2\text{O}$  is deposited in black needles, which increase in quantity as the temperature rises, but redissolve as the liquid cools.

The formation and stability of these sulphides depend on the strength of the solution of potassium sulphide, the relative proportion of mercuric sulphide, and the temperature. At a given temperature, the formation of one or the other double sulphide depends on the strength of the solution, and with a certain degree of concentration of the solution and a certain proportion of mercuric sulphide, one or the other double sulphide can be formed by raising or lowering the temperature. If a cold solution containing crystals of the compound  $\text{HgS}, \text{K}_2\text{S}, 7\text{H}_2\text{O}$  is mixed with mercuric sulphide, the white crystals gradually disappear and are soon completely converted into black needles.

C. H. B.

**Transformation of Prismatic Antimony Oxide into the Octahedral Oxide.** By M. GUNTZ (*Compt. rend.*, **98**, 303).—The two modifications of antimony oxide dissolve in hydrofluoric acid with development of unequal amounts of heat, namely, 9.5 cal. for octahedric oxide, and 10.1 cal. for the prismatic; whence it may be concluded that the transformation of the one form into the other develops heat = 0.6 cal.

R. R.

**Determination of the Atomic Weight of Chromium.** By H. BAUBIGNY (*Compt. rend.*, **98**, 146—148).—The author has determined the atomic weight of chromium by igniting the pure sulphate (this vol., 558). One series of experiments gave a mean of 52.03; whilst another series with the sulphate prepared from chlorochromic acid, gave 52.16; the author considers the latter to be the more trustworthy.

R. R.

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### Mineralogical Chemistry.

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**Samarskite from Berthier County, Quebec.** By J. T. DONALD (*Chem. News*, **49**, 259—260).—Samarskite has not hitherto been found in Canada. The following is the description of the specimen examined:—It consisted of irregular brownish-black (almost black) opaque amorphous fragments (sp. gr. 4·9478), with a sub-metallic shining lustre; in parts iridescent. It is brittle, fracture uneven; streak greyish-brown; hardness about 6, and fuses between 4—4·5°, decrepitating and giving off a small quantity of acid water in a closed tube. When heated with concentrated sulphuric acid, it is decomposed readily and completely. Analysis gave:—

Nb <sub>2</sub> O <sub>5</sub> , Ta <sub>2</sub> O <sub>5</sub> .	SnO <sub>2</sub> .	YO.	Ce <sub>2</sub> O <sub>3</sub> .	U <sub>2</sub> O <sub>3</sub> .	MnO.	FeO.	CaO.
55·41*	0·10	14·34	4·78	10·75	0·51	4·83	5·38
MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Fl.	H <sub>2</sub> O.			
0·11	0·39	0·23	trace	2·21 = 99·04			

Another specimen has been found very similar to the above. Its sp. gr. (5·305) is, however, higher. This mineral is not rare in the locality mentioned. D. A. L.

**Artificial Pseudomorphism of Silica.** By A. GORGEU (*Compt. rend.*, 98, 1281—1282).—When crystals of artificial fayalite are calcined at a cherry-red heat for seven or eight hours with exposure to air, the ferrous oxide is completely oxidised, and the transparent grey crystals of the original silicate become black and opaque, but retain their original form. On treatment with concentrated boiling hydrochloric acid, the whole of the silica is left undissolved. This insoluble silica is transparent, has a pale yellow colour due to the presence of a small quantity of ferric oxide, and contains from 4 to 5 per cent. of water, which it gives off when heated. It dissolves in a boiling solution of sodium carbonate. This silica retains the exact form of the original crystals of fayalite. When examined in the dry state with polarised light, it behaves like a doubly refracting substance, but if placed in water, it loses this property, and behaves like a singly refracting substance; it is, in fact, not truly crystalline.

The same pseudomorphism can be obtained by treating artificial knebelite in the same manner, but the silica obtained in this way from natural knebelite, which only occurs in lamellar masses, does not possess the same property. Tephroite, rhodonite, hypersthene, diallage, hornblende, &c., do not sensibly oxidise when roasted in the air, and do not give rise to a pseudomorphism of silica under the above conditions. C. H. B.

**Mineral Water at Brucourt.** By C. CLOËZ (*Compt. rend.*, 98, 1282—1285).—The mineral water at Brucourt (Calvados) about 4 kilom. south of Dives, was described by Musner in 1637, and by Lepecq de la Clôture in 1776, and the water has been frequently analysed, the last analysis being that of O. Henry in 1862. Since that time, however, alterations have been made in the spring, whereby infiltration has been prevented, and the flow of water considerably increased. The sample examined was collected on April 1st, 1884. The water has a neutral reaction, is very transparent, and keeps well in bottles. The following results were obtained, in grams per litre:—

Total residue at 180°.	Na <sub>2</sub> O.	K <sub>2</sub> O.	MgO.	CaO.	FeO.	Al <sub>2</sub> O <sub>3</sub> and SiO <sub>2</sub> .
2·3305	0·1122	0·0151	0·3006	0·4933	0·0213	0·0710
	SO <sub>3</sub> .	Cl.	CO <sub>2</sub> .			
	0·8156	0·1802	0·5076			

\* Almost entirely Ta<sub>2</sub>O<sub>5</sub>.



or arranging these constituents conventionally—

	Per litre.
Free carbonic anhydride ..	185 c.c.
Sodium chloride .....	0·2113 gram
Potassium „ .....	0·0238 „
Magnesium „ .....	0·0477 „
„ sulphate.....	0·5280 „
Calcium „ .....	0·7881 „
„ bicarbonate ....	0·4880 „
Magnesium „ ....	0·3815 „
Ferrous „ ....	0·0526 „
Alumina and silica .....	0·0710 „
	<hr/>
	2·5920 „

The water is therefore both a magnesian and a chalybeate water, and is the only spring in France which combines both these qualities. Moreover, three litres of the water yield very distinct traces of iodine, and the presence of this element doubtless has considerable influence on the therapeutic action of the water.

C. H. B.

## Organic Chemistry.

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**Formation of Methyl Iodide and Methylene Iodide from Iodoform.** By P. CAZENEUVE (*Compt. rend.*, **98**, 369—370).—When water (2 parts) is added to a mixture of powdered iodoform with an equal weight of iron reduced by hydrogen (5 parts of each), and the whole slightly heated, iodine is displaced by the nascent hydrogen and a mixture of methyl iodide and methylene iodide is obtained, which are easily separated by distillation in a vacuum; in this way the decomposition of the methylene iodide by heat is avoided.

The hydrogenating action is progressive; acetylene, methylene iodide, methyl iodide, and hydrogen, being produced in succession.

R. R.

**Action of Arsenious Anhydride on Glycerol.** By H. JACKSON (*Chem. News*, **49**, 258).—When about equal parts of arsenious anhydride and glycerol (1 mol. of former to 2 mols. of latter) are heated in a sealed tube at 250° for two hours, the arsenic displaces the hydroxylic hydrogen-atoms, and water is eliminated according to the equation:  $2C_3H_5(OH)_3 + As_2O_3 = 2C_3H_5AsO_3 + 3H_2O$ . The arsenious glyceride formed in this manner is a colourless, transparent, very deliquescent, vitreous solid, soluble in absolute alcohol and glycerol, but decomposed by water into glycerol and arsenious anhydride. It softens at 100°, is liquid at 200°, and when dry is not decomposed until the temperature exceeds 290°.

D. A. L.

**Reduction of Erythrol by Formic Acid.** By A. HENNINGER (*Compt. rend.*, **98**, 149—151).—The action of formic acid on the polyhydric alcohols is to successively displace the OH-groups in pairs by formyl, giving rise to unsaturated compounds, and the author found that this reduction is necessarily preceded by the formation of a formin. When erythrol is boiled for six hours with two and a half times its weight of formic acid, and the excess of acid is distilled off at 200°, the crystalline residue contains 49 to 50 per cent. of combined formic acid corresponding nearly in composition with a diformin,  $(\text{H.COO})_2\text{C}_4\text{H}_6(\text{OH})_2$ , but in reality is a mixture of formins, which may be separated by fractional crystallisation from alcohol and ether. Amongst these is the tetraformin  $(\text{H.COO})_4\text{C}_4\text{H}_6$ , which is obtained in long silky needles, almost insoluble in cold alcohol, still less in water and in ether, and fusible at 150°. Hot water saponifies it with regeneration of erythrol. When the mixture of formins is distilled at 250°, carbonic anhydride, carbonic oxide, and a gas identical with Caventou's crotonylene,  $\text{C}_4\text{H}_6$ , are evolved, and a complex liquid passes over into the receiver, consisting of water, formic acid, crotonaldehyde, and two new substances, namely, *crotonylene glycol*,  $\text{C}_4\text{H}_6(\text{OH})_2$ , and a liquid ( $\text{C}_4\text{H}_6\text{O}$ ) boiling at 67°, for which the author proposes the name of *dihydrofurfurane*. The reaction also gives rise to *erythrane*,  $\text{C}_4\text{H}_8\text{O}_3$ , the hitherto unknown first anhydride of erythrol.

R. R.

**Hydroxycellulose and Phenylhydrazine.** By C. F. CROSS and E. J. BEVAN (*Chem. News*, **49**, 257—258).—The authors remark that in addition to reactions of the salts of phenylhydrazine already described, the hydrochloride of the base gives other characteristic reactions. When warmed with hydroxycelluloses, for example, it gives a deep yellow, and with lignose a dull yellow coloration.

D. A. L.

**Action of Hydrobromic Acid on the Ethereal Salts of Hydroxyacids.** By A. FÖLSING (*Ber.*, **17**, 484—486).—A series of experiments on the action of hydrobromic acid on the methyl and ethyl salts of methyl- and ethyl-glycollic and methyl- and ethyl-salicylic acids, shows that the reaction takes place in two stages, the alcoholic radical in the carboxyl group being expelled first. Methyl ethylglycollate yields first methyl bromide and ethylglycollic acid, and finally ethyl bromide and glycollic acid. Methyl ethylsalicylate behaves in a similar manner.

W. C. W.

**Boiling Points of the Ethereal Salts of Glycollic and Salicylic Acids.** By A. FÖLSING (*Ber.*, **17**, 486—488).—The author has redetermined the boiling points of the ethers of glycollic and salicylic acids, and finds that Schreiner's numbers (*Annalen*, **197**, 1) are invariably too high. The correct results are shown below:—

	$\text{CH}_3$ .	$\text{C}_2\text{H}_5$ .
Methylglycollic acid .....	127°	131°
Ethylglycollic „ .....	148	152
Methylsalicylic „ .....	228	235
Ethylsalicylic „ .....	245	251

The displacement of methyl by ethyl in the carboxyl-group raises the boiling point from  $4^{\circ}$  to  $6^{\circ}$ , but in the alcoholic or phenolic hydroxyl it raises it about  $20^{\circ}$ .

The difference in boiling points diminishes with a reduced pressure.

W. C. W.

**Transformation of Glyoxal into Glycollic Acid.** By DE FORCRAND (*Compt. rend.*, **98**, 295—297).—In preparing glyoxal, the author substitutes aldehyde for the alcohol first used by Debus. The crude product of the action of nitric acid on aldehyde is evaporated, dissolved in water, neutralised by calcium carbonate, and filtered. Glycollic and glyoxylic acids are then precipitated from the filtrate by basic lead acetate, and from this second filtrate the calcium is exactly precipitated by oxalic acid; a liquid is thus obtained containing nothing but acetic acid and glyoxal. This, when evaporated over the water-bath, yields an amorphous residue which, after being dried in a vacuum at a temperature not exceeding  $120^{\circ}$ , consists of nearly pure glyoxal.

Glyoxal dissolves readily in cold water with a very partial transformation into glycollic acid, but at  $150^{\circ}$  the quantity so transformed may amount to one-third of the glyoxal; hence the difficulties attending the preparation of glyoxal. The paper gives determinations of the thermic phenomena accompanying this transformation. R. R.

**Derivatives of Orthoxylylene.** By A. BAEYER and C. PAPE (*Ber.*, **17**, 447—448).—Orthoxylyl cyanide,  $C_{10}H_8N_2$ , is prepared by the action of orthoxylyl bromide on potassium cyanide dissolved in a mixture of alcohol and water. The cyanide is extracted from the mixture by ether. It is a crystalline salt melting at  $60^{\circ}$ , and soluble in alcohol and ether. On saponification with alkalis or acids, it yields *phenyleneorthodiacetic acid*,  $C_6H_4(CH_2.COOH)_2$ , crystallising in needles, which melt at  $150^{\circ}$ . It is soluble in alcohol, ether, and in hot water. The silver salt,  $C_{10}H_8O_4Ag_2$ , is insoluble in water.

W. C. W.

**English and Scotch Coal-tar Xylenes.** By I. LEVINSTEIN (*Ber.*, **17**, 444—446).—Orthoxylylene is invariably present in English and Scotch coal-tar xylenes. Metaxylylene and the non-aromatic hydrocarbons in commercial xylene are estimated by the following process: 100 c.c. of the xylene is boiled with 40 c.c. of nitric acid (sp. gr. 1.44) diluted with 60 c.c. of water, until the para- and orthoxylylene is completely oxidised. The acid is run off by means of a separating funnel. The hydrocarbons are washed with caustic soda and distilled in a current of steam. The distillate consisting of metaxylylene and non-aromatic hydrocarbons is first measured and afterwards well shaken with strong sulphuric acid ( $1\frac{1}{2}$  vols.) for half an hour; this dissolves the metaxylylene and leaves the other hydrocarbons.

In order to estimate the paraxylylene, 100 c.c. of crude xylene are shaken with 120 c.c. of strong sulphuric acid to dissolve ortho- and metaxylylene.

The volume of the residual paraxylylene and other hydrocarbons having been noted, the liquid is then treated with an equal bulk of fuming

sulphuric acid containing 20 per cent. of  $\text{SO}_3$  to dissolve the paraxylene. The difference between the volume of residual hydrocarbons and the former volume gives the amount of paraxylene. The percentage of orthoxylene is obtained by deducting the volume of para- and metaxylene and that of the non-aromatic hydrocarbons from 100, the volume of crude xylene originally taken. This method would not yield correct results with a very impure product, as toluene and cymene, &c., are attacked by nitric and sulphuric acids: in such cases it is advisable to convert the ortho- and metaxylenesulphonic acids into their sodium salts, which can be separated by recrystallisation.

The following table shows the composition of different specimens of crude xylene.

	Sp. gr. at 19°.	B. p.	Meta- xylenes.	Para- xylenes.	Ortho- xylenes.	Non-aromatic hydrocarbons.
English.....	0·8629	134—140°	87	6	4	3
„ .....	—	140—143	87	4	6	3
„ .....	0·866	138—141	79	3	15	3
Scotch.....	0·8574	134—140	72	8	12	8
„ .....	—	139—141	70	5	15	10
Mixture of English and Scotch ....	0·8605	134—141	81	10	3	6
Mixture of English and Scotch ....	—	136—142	86	6	4	4
Mixture of English and Scotch ....	0·8600	136—142	85	6	3	6
Gas xylene .....	—	138—144	47	8	13	26

W. C. W.

**Triphenylmethylaniline.** By O. NAUEN (*Ber.*, 17, 442—443).—Triphenylmethylaniline is prepared by passing ammonia gas into a mixture of triphenylmethane chloride and naphthalene at 130°. The product is extracted with light petroleum and the triphenylmethylaniline is precipitated from this solution by hydrochloric acid gas. The precipitate is dissolved in dilute hydrochloric acid, and the liquid shaken up with ether. The amine is reprecipitated on adding soda to the acid solution. Triphenylmethylaniline crystallises in prisms which dissolve freely in alcohol, ether, benzene, and carbon bisulphide. It melts at 102°, and decomposes on distillation. The hydrochloride forms needle-shaped crystals sparingly soluble in water.

On boiling triphenylmethylaniline with acetic anhydride, it is decomposed, forming acetamide and triphenylcarbinol. W. C. W.

**Isomeric Isobutylorthamidotoluenes.** By J. EFFRONT (*Ber.*, 17, 419—420).—When orthotoluidine hydrochloride and isobutyl alcohol are heated at 300°, an isobutylorthamidotoluene is formed in large quantities; this is isomeric with the amine Erhardt obtained by heating isobutyl alcohol and orthotoluidine with zinc chloride. The amine was converted into a nitrile from which isobutylortho-

toluic acid,  $C_6H_3Me(C_4H_9).COOH$ , was obtained in needle-shaped crystals melting at  $140^\circ$ .

The amine was also converted into a diazo-chloride, which on reduction with stannous chloride yields isobutyltoluene (b. p.  $185^\circ$ ), probably identical with Kelbe's meta-isobutyltoluene (*Ber.*, **16**, 2560).  
W. C. W.

**Bromophenols.** By E. WERNER (*Compt. rend.*, **98**, 1333—1336).—*Monobromophenol*,  $C_6H_5BrO$ , obtained by the action of bromine vapour on an equivalent quantity of crystallised phenol, boils at  $137^\circ$  under a pressure of 28 mm., and melts at  $64^\circ$ , but remains liquid at  $13^\circ$ . Its heat of neutralisation when liquid at  $13^\circ = +7.43$  cal.; when solid at  $11^\circ = +4.42$  cal.; when dissolved  $= +8.09$ . From these numbers it follows that its molecular heat of fusion at  $12^\circ = -3.01$  cal.; its heat of solution when liquid  $= +0.63$  cal.; when solid  $= +3.67$  cal. Specific heat of the liquid between  $18^\circ$  and  $77^\circ = 0.3157$ ; molecular heat  $= +54.6$  cal.

*Dibromophenol* obtained by the same method as the preceding compound, using twice as much bromine, boils at  $154^\circ$  under a pressure of 47 mm., and melts at  $40^\circ$ , but remains superfused at  $12^\circ$ . Its heat of neutralisation when liquid  $= +8.46$  cal.; when solid  $+4.93$  cal., whence the molecular heat of fusion at  $12^\circ = -3.52$  cal. Specific heat of the liquid between  $18.5^\circ$  and  $73^\circ = 0.2436$ ; molecular heat  $= 61.4$ .

*Tribromophenol* prepared in the ordinary way, melts at  $92^\circ$ . Its heat of neutralisation when solid at  $13^\circ, = +5.41$  cal.

The solubility of the three compounds at  $15^\circ$  is as follows:—

	Per litre.
$C_6H_5BrO$ .....	14.22 grams
$C_6H_4Br_2O$ .....	1.94   "
$C_6H_3Br_3O$ .....	0.07   "

It will be seen that the solubility decreases as the amount of bromine increases, but that the heat of fusion and heat of solution increase with the amount of bromine. In the solid state, phenol and its bromo-substitution derivatives have practically the same heat of neutralisation, but in solution they would probably show differences similar to those observed in the case of other phenol derivatives.

C. H. B.

**Azo- and Disazo-compounds of Cresols.** By E. NÖLTING and O. KOHN (*Ber.*, **17**, 351—369).—Paracresol unites with diazo-compounds to form substances in which the diazo-residue occupies the ortho-position as regards the hydroxyl-group. Neither disazo- nor nitroso-derivatives have been obtained.

Ortho- and meta-cresol form oxyazo-compounds with diazo-derivatives. The azo-group occupies the para-position. They also yield disazo-compounds in which the azo-groups occupy the para- and ortho-positions as regards the hydroxyl-group.

*Phenylazoparacresol*,  $Ph.N_2.C_6H_3Me.OH[1:4]$ , described by Mazzara (*Gazzetta*, **9**, 424; *Ber.*, **12**, 2367), is best prepared by pouring diazobenzene chloride into a strongly alkaline solution of paracresol. The mixture must be cooled down to  $0^\circ$  during the reaction. Phenylazo-

paracresol forms orange-coloured plates (m. p.  $108^{\circ}$ ) soluble in benzene. The *acetic* derivative,  $\text{Ph.N}_2\text{C}_6\text{H}_3\text{Me.OAc}$ , crystallises in yellow needles which melt at  $67.5^{\circ}$ , and are freely soluble in alcohol, ether, chloroform, and acetone. It is slowly saponified by alkaline carbonates. The *benzoic* derivative melts at  $113^{\circ}$ . It is soluble in ether, chloroform, hydrocarbons, and hot alcohol. It is slowly attacked by free alkalis, but not by carbonates.

*Azobenzene-azoparacresol*,  $\text{Ph.N}_2\text{C}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_3\text{Me.OH}$ , is prepared by adding sodium nitrite to an ice-cold solution of amidoazobenzene hydrochloride containing free hydrochloric acid. The mixture is poured into an alkaline solution of paracresol. After recrystallising the precipitate from glacial acetic acid, azobenzene-paracresol is obtained in brown needle-shaped crystals, which melt at  $160^{\circ}$ , and are insoluble in alkalis at the ordinary temperature.

*Paratolylazoparacresol*,  $\text{C}_6\text{H}_4\text{Me.N}_2\text{C}_6\text{H}_3\text{Me.OH}$  [ $\text{CH}_3 : \text{N}_2 = 4 : 1$ , and  $\text{OH} : \text{CH}_3 = 1 : 4$ ], crystallises in plates which melt at  $112^{\circ}$ . It is soluble in ether, chloroform, hydrocarbons, and in hot alcohol. The acetic and benzoic derivatives crystallise in yellow needles which melt at  $91^{\circ}$  and  $95^{\circ}$  respectively.

*Parasulphophenylazoparacresol*,  $\text{C}_6\text{H}_4(\text{SO}_3\text{H}).\text{N}_2\text{C}_6\text{H}_3\text{Me.OH}$ , crystallises in scales of yellowish-brown colour, which are decomposed by heat. The compound is soluble in water, but dissolves very sparingly in cold alcohol. The acid potassium, sodium, magnesium, and barium salts of this body crystallise in plates of a yellow or yellowish-brown colour. The magnesium and barium salts are almost insoluble in cold water. The acid and its salts dye wool and silk yellow. This acid is also formed by the action of fuming sulphuric acid (containing 60 to 65 per cent.  $\text{SO}_3$ ) on phenylazoparacresol.

*Phenylazoparacresolsulphonic acid*,  $\text{Ph.N}_2\text{C}_6\text{H}_3(\text{OH})\text{Me}(\text{SO}_3\text{H})$  [ $6 : 1 : 4 : 2$ ], formed by the action of paracresolsulphonic acid on an alkaline solution of diazobenzene chloride, crystallises in small plates, soluble in water. The acid sodium salt forms anhydrous plates of a reddish-brown colour. The acid solution dyes wool and silk orange.

As the paracresoldisulphonic acid prepared by Engelhardt and Latschinoff (*Zeitschr. f. Chem.*, 1869, 619) is converted into dinitro-paracresol by dilute nitric acid, the two sulphonic groups must occupy the position [2 : 6]. This acid does not combine with diazo-compounds.

*Metasulphoparatolylazoparacresol* yields crystalline salts. The anhydrous acid sodium salt is freely soluble. The barium salt containing 4 mols.  $\text{H}_2\text{O}$  is sparingly soluble.

On reduction with stannous chloride, the azoparacresol-derivatives yield amidoparacresol,  $\text{C}_6\text{H}_3(\text{OH})\text{Me.NH}_2$  [ $1 : 4 : 2$ ]; this melts at  $135^{\circ}$ , and sublimes without decomposition. It is soluble in alcohol, ether, and chloroform. Methenylamidoparacresol has been previously described by Hofmann and Miller (*Ber.*, 14, 573). The ethenyl-

derivative,  $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{CMe}$ , is a liquid boiling at  $218^{\circ}$ , and miscible

with alcohol and ether. It also dissolves in acids forming salts which easily decompose, yielding acetylamidoparacresol (m. p.  $160^{\circ}$ ).

*Azo-compounds of Orthocresol.*—*Phenylazorthocresol* forms glistening yellow plates melting at  $130^{\circ}$  and soluble in alcohol, ether, chloroform, and hydrocarbons, and also in caustic alkalis. It is formed, together with the disazo-compound  $(\text{PhN}_2)_2\text{C}_6\text{H}_2\text{Me.OH}$ , by the action of diazobenzene chloride on an alkaline solution of orthocresol. The two bodies are separated by treatment with alcohol. *Phenylldisazo-orthocresol* crystallises in reddish-brown plates, which melt at  $115^{\circ}$ , and are very sparingly soluble in cold alcohol. The acetic derivative melts at  $121^{\circ}$ . *Phenylazorthacetylcresol* forms yellow plates, melting at  $82^{\circ}$ , and freely soluble in alcohol, ether, and chloroform. The benzoic derivative melts at  $110^{\circ}$ .

*Parasulphophenylazorthocresol* crystallises in needles which are sparingly soluble in alcohol and cold water. The acid sodium salt crystallises in scales containing 2 mols.  $\text{H}_2\text{O}$ , and the acid barium salt in plates containing 3 mols.  $\text{H}_2\text{O}$ . On reduction with stannous chloride, amidorthocresol,  $\text{C}_6\text{H}_3(\text{OH})\text{Me}(\text{NH}_2)$  [1 : 2 : 4] is produced. This body melts at  $175^{\circ}$ , and is obtained by sublimation in needles soluble in alcohol and ether.

The hydrochloride is very soluble in alcohol and water. When diazobenzene chloride acts on an alkaline solution of metacresol, *phenylazometacresol* remains in solution, and the disazo-compound is precipitated. The azo-compound is deposited on acidifying the alkaline filtrate. *Phenylazometacresol* crystallises in yellow needles melting at  $109^{\circ}$  and soluble in alcohol. On reduction, it yields amido-metacresol melting at  $151^{\circ}$ .

*Sulphorthotolylazometacresol*,  $\text{C}_6\text{H}_3\text{Me}(\text{SO}_3\text{H}).\text{N}_2.\text{C}_6\text{H}_3\text{Me.OH}$ , forms small reddish-brown crystals soluble in water. The acid sodium and barium salts are anhydrous. The former is freely, and the latter sparingly soluble in cold water. The azo-compounds of ortho- and metacresol dye silk and wool orange.

*Phenylldisazometacresol*  $(\text{PhN}_2)_2\text{C}_6\text{H}_2\text{Me.OH}$ , can also be prepared by pouring diazobenzene into an alkaline solution of metacresol. It is deposited from a hot alcoholic solution in plates which melt at  $149^{\circ}$ , and dissolve freely in ether, chloroform, and benzene. The acetic derivative melts at  $157^{\circ}$ .

*Phenylldisazomethoxybenzene*  $(\text{PhN}_2)_2\text{C}_6\text{H}_3.\text{OMe}$  (m. p.  $110^{\circ}$ ), and the corresponding acetoxy-derivative (m. p.  $116^{\circ}$ ) and benzoyl-derivative (m. p.  $139^{\circ}$ ), yield on reduction with zinc-dust and acetic acid, diamido-derivatives in which the amido-groups occupy the meta-position. This shows that in phenylldisazophenol  $\text{OH} : \text{N}_2\text{Ph} : \text{N}_2\text{Ph}_2 : = 1 : 2 : 4$ .  
W. C. W.

**Molecular Changes of Hydrazo-compounds.** By G. SCHULTZ (*Ber.*, 17, 463—478).—An alcoholic solution of acetylamidoazobenzene is converted into a hydrazo-compound by the action of ammonium sulphide. This substance forms crystalline plates (m. p.  $146^{\circ}$ ) soluble in alcohol and ether. It is turned blue by strong hydrochloric acid, and is decomposed by stannous chloride into aniline and paraphenylendiamine.

When paradichlorazobenzene is treated with stannous chloride, it takes up 2 atoms of hydrogen, forming a diphenyl base, which crys-



tallises in violet-coloured plates (m. p.  $60^{\circ}$ ). The base gives a violet coloration with strong sulphuric acid, red with ferric chloride, and yellow with bleaching powder.

Metadichlorazobenzene is converted into dichlorodiamidodiphenyl (m. p.  $163^{\circ}$ ) by stannous chloride.

*Metadichloroxyazobenzene* (m. p.  $114^{\circ}$ ) is formed, together with a small quantity of metadichlorazobenzene, when metadichloroxybenzene is dissolved in strong sulphuric acid. It is deposited from alcohol in brown scales, which melt at  $114^{\circ}$ . Stannous chloride converts paradibromazobenzene into parabromaniline and dibromodiamidodiphenyl. The latter body crystallises in red scales (m. p.  $108^{\circ}$ ), which dissolve in dilute acids and in absolute alcohol. By the action of nitrous acid on the alcoholic solution, the azoimido-compound,  $C_{12}H_7N_3Br_2$  (m. p.  $206^{\circ}$ ), is produced.

*Benzene-azoparatoluene*,  $C_6H_4Me.N_2.Ph$ , is prepared by adding an alcoholic solution of nitrous acid to an alcoholic solution of amido-benzeneazoparatoluene. The mixture is left at rest for 12 hours, and is then distilled with soda-lye. Benzeneazotoluene forms orange-red plates, which melt at  $63^{\circ}$  and dissolve freely in alcohol. It is decomposed by treatment with stannous chloride, yielding aniline, paratoluidine, a crystalline compound melting at  $116^{\circ}$ , volatile in steam, and a small quantity of a base which does not distil in a current of steam.

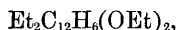
*Orthazotoluene* crystallises in monoclinic plates of a reddish-brown colour melting at  $55^{\circ}$ ; it is soluble in alcohol and ether. Hydrazotoluene melts at  $146^{\circ}$ . The *tolidine* derived from it has been described by Petrieff. When the alcoholic solution of orthotolidine is treated with nitrous acid, a nitrogenous compound is deposited in needle-shaped crystals melting at  $287^{\circ}$ ; the mother-liquor contains ditolyl- and diethyl ditolyl ether melting at  $156^{\circ}$ . Ditolyl yields isophthalic acid on oxidation, but by the cautious addition of chromic acid to an acetic acid solution of ditolyl, diphenyldicarboxylic acid melting at  $193^{\circ}$  may be obtained.

*Orthotolueneazometatoluene*,  $C_6H_4Me.N^2.N^1.C_6H_4Me^3$ , is prepared by the action of an alcoholic solution of nitrous acid on amidoazotoluene (from orthotoluidine) at  $0^{\circ}$ . When stannous chloride acts on it in alcoholic solution, *orthometatolidine* is formed. It yields crystalline salts. It is converted into ditolyl by an alcoholic solution of nitrous acid: the hydrocarbon boils at  $270^{\circ}$ , and is oxidised by chromic acid to isophthalic acid. An alcoholic solution of parazotoluene is slowly converted into tolidine at the ordinary temperature by the action of an acid solution of stannous chloride. The ditolyl obtained by treating an alcoholic solution of the tolidine with nitrous acid, crystallises in needles or plates, which melt at  $91^{\circ}$ . The crystals dissolve freely in ether and alcohol. On oxidation, the hydrocarbon yields an acid which melts at  $273^{\circ}$ , and is insoluble in water.

Orthazoethylbenzene is prepared by the action of zinc-dust on a solution of orthonitroethylbenzene in alcoholic potash. After the addition of the zinc-dust, the mixture is boiled for six hours in a flask provided with a reversed condenser, and is then filtered hot. The

alcohol is removed from the filtrate by distillation, and the residue is poured into water. The aqueous mixture is extracted with ether, and the extract is shaken with dilute hydrochloric acid and then evaporated, when the azo-compound is obtained in dark-red quadratic needles or prisms,  $a:c = 1:0.3455$ . The crystals melt at  $46.5^\circ$ , and dissolve freely in hot alcohol.

The base which is produced by the reduction of azoethylbenzene with stannous chloride does not crystallise, but its acetic derivative,  $\text{NH}_4\text{Ac} \cdot \text{C}_6\text{H}_5\text{Et} \cdot \text{C}_6\text{H}_5\text{Et} \cdot \text{NH}_4\text{Ac}$ , crystallises in needles which melt at  $307^\circ$ . It dissolves in acetic acid, but is very sparingly soluble in alcohol. When the alcoholic solution of the base is treated with nitrous acid, a small quantity of a liquid hydrocarbon is produced, together with diethylphenyldiethyl oxide, melting at  $120^\circ$ .



*Parazoethylbenzene* is deposited from alcohol in orange-red plates or prisms, which melt at  $63^\circ$  and boil above  $340^\circ$ . On reduction with stannous chloride in presence of sulphuric acid, it yields paramidoethylbenzene and an unstable diphenyl base,  $\text{C}_{16}\text{H}_{20}\text{N}_2$ .

Azometaxylenes could not be converted into a diphenyl base.

*Azomesitylene* prepared by oxidising an alkaline solution of mesidine hydrochloride with potassium ferricyanide, crystallises in thin needles melting at  $75^\circ$ , soluble in hot alcohol. Attempts to obtain a diphenyl base from this body failed.

No azo-compound could be obtained from amidoazonaphthalene or from nitroquinoline.

W. C. W.

**An Aromatic Diketone.** By E. LOUISE (*Compt. rend.*, **98**, 151—153).—In a recent paper the author has already described the preparation of the ketone benzoylmesitylene by the action of benzoic chloride on mesitylene in presence of aluminium chloride. By dissolving benzoylmesitylene in benzoic chloride, and maintaining the liquid at  $150^\circ$ , while aluminium chloride is gradually added until the evolution of hydrochloric acid ceases (about 24 hours are required), a black mass is obtained; this, after treatment first with hot water and a little potassium hydroxide to remove unaltered benzoic chloride, is treated with a mixture of alcohol and ether, which leaves the carbonaceous matters undissolved. The filtered solution is set aside to crystallise, and the crystals are purified by distillation in a vacuum at  $300^\circ$ . The analysis corresponds with the formula  $\text{C}_{23}\text{H}_{20}\text{O}_2$ , or dibenzoylmesitylene,  $\text{C}_6\text{HMe}_3(\text{COPh})_2$ . This body forms well defined, transparent, colourless crystals, soluble in alcohol, ether, light petroleum, &c., and melts at  $117^\circ$ .

R. R.

**Pure Benzoic Acid from Urine.** By T. S. DYMOND (*Pharm. J. Trans.* [3], **14**, 463—464).—Benzoic acid, prepared from urine (hippuric acid), crystallises in plates, and has an unpleasant urine-like odour. By careful sublimation it can be deprived of this odour, and is obtained pure, crystallising in the same way as benzoic acid obtained from gum-benzoin.

D. A. L.

**A Nitrogenised Colloid derived from Amidobenzoic Acid.**

By E. GRIMAUZ (*Compt. rend.*, **98**, 231—234).—The white powder produced by the action of phosphorus pentachloride on amidobenzoic acid is dissolved in ammonia, filtered, and evaporated in a vacuum at ordinary temperatures. The amidobenzoic colloid at first forms a thick jelly, which, by drying, is converted into transparent, yellowish, tasteless, indorous plates resembling the albumin of serum. It swells up in cold water and slowly dissolves, but is readily soluble in hot water. It may be heated to 100° without losing its solubility in water; but if the solution be evaporated to dryness on the water-bath, the residue, although retaining the same appearance, becomes altogether insoluble, and in this respect resembles albumin. It dissolves however in ammonia, in sodium phosphate, and in alkaline solutions. A 2 per cent. solution of the amidobenzoic colloid behaves like the nitrogenised colloids derived from living organisms; it is precipitated by acids, and is redissolved with difficulty by acetic acid; hot nitric acid dissolves it with a yellow coloration, changed to orange by alkalis. An excess of lime-water precipitates the solution, but if only one-twentieth of lime-water is added, the liquid remains clear, or becomes merely opalescent; it then becomes coagulable by heat, forming a stiff jelly. Dilute ammonium chloride solution, saturated solution of sodium chloride, a 1 per cent. solution of magnesium sulphate, and certain other saline solutions, have the same effect as lime-water; that is, when added to the cold solution in quantity insufficient to render it turbid, they confer upon it the property of coagulating by heat. At about 50° the liquid becomes opalescent, then milky, and the coagulum forms between 70° and 80°, the temperature varying with the proportion of salt that has been added. The effect of the latter, however, is much modified by various circumstances, as dilution, the presence of other salts, &c. If the quantity of the coagulating salt be insufficient to produce the effect even at the boiling point, yet by passing carbonic anhydride through the liquid either before or after the addition of the salt, the solution becomes coagulable by heat. This fact appears to have a relation with Mathieu and Urbain's experiments on the part played by carbonic anhydride in the coagulation of albumin (*Bull. Soc. Chim.*, **21**, 181; **22**, 484). The coagulum formed by the action of acid or of alkaline salts is soluble in ammonia; while that produced by salts of calcium, barium, or magnesium, is not. The phenomena of coagulation in the amidobenzoic colloid being the same as those observed in the coagulation of albuminoids, the latter, when separated from the organism, must be subject to physico-chemical laws only.

R. R.

**Bismuth Salicylate.** By L. WOLFF (*Pharm. J. Trans.* [**3**], **14**, 508).—This substance may be obtained pure by either of the following methods:—By decomposing a glycerol solution of crystalline bismuthous nitrate with a concentrated solution of sodium salicylate, bismuthyl salicylate, sodium nitrate, nitric acid, salicylic acid, and water being produced; the latter products are removed by successive washing with water, hot water, and alcohol. Or by boiling bismuthyl nitrate,  $\text{BiONO}_3 \cdot \text{H}_2\text{O}$ , with a concentrated solution of sodium salicylate; the precipitate is well washed with hot water.

Bismuthyl salicylate,  $\text{BiOC}_7\text{H}_5\text{O}_3$ , forms slightly pinkish amorphous granules, insoluble in water, glycerol, alcohol, and ether; soluble, probably with decomposition, in acids. It burns rapidly on platinum foil. D. A. L.

**Phenylisocrotonic Acid and Nitric Acid. Phenylnitroethylene.** By H. ERDMANN (*Ber.*, 17, 412—415).—*Phenylnitroethylene*,  $\text{CHPh}:\text{CH}.\text{NO}_2$ , is formed when phenylisocrotonic acid is slowly added to fuming nitric acid which has been cooled down below zero. An unstable acid is formed which is dissolved in dilute sodium hydroxide, and reprecipitated by hydrochloric acid. The acid is rapidly decomposed with evolution of carbonic anhydride. On distillation in a current of steam, yellow needle-shaped crystals of phenylnitroethylene melting at  $58^\circ$  are obtained. This compound is identical with that which Priebs (*Ber.*, 16, 2591) prepared by the action of nitromethane on benzaldehyde. W. C. W.

**Constitution of Phenylparaconic Acid.** By H. ERDMANN (*Ber.*, 17, 415—418).—On boiling ethylic phenylparaconate with dilute ammonia, it is converted into ethylic phenylitamalate. At  $150^\circ$ , phenylparaconic acid is decomposed into  $\alpha$ -naphthol and phenylisocrotonic acid, but the ethylic salt boils above  $360^\circ$  without decomposition. The author regards these facts, first, as evidence in favour of the hypothesis that the carbonic anhydride which escapes when phenylparaconic acid is decomposed is derived from the carboxyl-group, and not from the lactone ring; and, secondly, as evidence in favour of the formulæ proposed by Fittig and Jayne for phenylparaconic acid:—



Phenylitamalic acid.

Phenylparaconic acid.

W. C. W.

**Oxalamido-acids.** By H. SCHIFF (*Ber.*, 17, 401—404).—When metamidobenzoic acid is dissolved in a warm mixture of absolute alcohol and ethyl oxalate, colourless crystals of *ethyl metabenzamoxalate*,  $\text{COOH}.\text{C}_6\text{H}_4.\text{NH}.\text{CO}.\text{COOEt}$ , are deposited. The crystals melt at  $225^\circ$  with decomposition, forming ethyl oxalate and *metoxalyldibenzamic acid*,  $\text{C}_2\text{O}_2(\text{NH}.\text{C}_6\text{H}_4.\text{COOH})_2$ . An alcoholic solution of ethyl oxalate converts metamidobenzamide into *ethyl metabenzamoxalate*,  $\text{CONH}_2.\text{C}_6\text{H}_4.\text{NH}.\text{CO}.\text{COOEt}$ , a crystalline compound melting at  $191.5^\circ$ , soluble in alcohol. An excess of amidobenzamide converts the compound into the *diamide* of *metoxalyldibenzamic acid*,  $\text{C}_2\text{O}_2(\text{NH}.\text{C}_6\text{H}_4.\text{CONH}_2)_2$ , a white infusible and sparingly soluble powder.

*Malonyldibenzamic acid*,  $\text{C}_3\text{H}_2\text{O}_2(\text{NH}.\text{C}_6\text{H}_4.\text{COOH})_2$ , and *ethyl metabenzammalonate*,  $\text{COOH}.\text{C}_6\text{H}_4.\text{NH}.\text{CO}.\text{CH}_2.\text{COOEt}$ , are formed when metamidobenzoic acid is boiled with ethyl malonate diluted with alcohol. The former is deposited from the boiling mixture in the form of a white powder, and the latter is deposited in silvery needles on evaporating the mother-liquor. These crystals melt at  $172^\circ$ , and

decompose at the same temperature, forming malonyldibenzamic acid and ethyl malonate.

Ethyl oxalate slowly dissolves alanine with evolution of carbonic anhydride. The solution, in course of time, deposits crystals of ethylimidodiethyldioxamide,  $\text{NEt}(\text{CO}.\text{CO}.\text{NHEt})_2$ . This compound melts between  $135^\circ$  and  $138^\circ$  with decomposition. The mother-liquor appears to contain several acids which have not yet been isolated.

W. C. W.

**Action of Thiocarbimides on Amido-acids.** By O. ASCHAN (*Ber.*, 17, 420—431).—The author has obtained compounds isomeric with the phenylthiohydantoin and hydantoic acid of P. Meyer (*Ber.*, 10, 1965; and 14, 1660), in which the sulphur-atom only is attached to a carbon-atom, and he proposes to distinguish these compounds as “phenylsulphhydantoin,” “phenylsulphhydantoic acid,” &c.,



From the results of his experiments, the author concludes that aromatic thiocarbimides act on those amido-acids of the fatty series which contain the amine-group in the  $\alpha$ -position, forming an homologous series of substituted sulphhydantoins.

These bodies are decomposed by boiling with alcoholic potash. They take up a molecule of water, yielding sulphhydantoic acids, which are very unstable, losing a molecule of water at the ordinary temperature forming sulphhydantoins.

Aromatic and non-aromatic thiocarbimides act on metamidobenzoic acid, forming sulphuramidobenzoic acids, which are stable compounds, e.g.:—

*Metaphenylthiamidobenzoic acid*,  $\text{NHPh}.\text{CS}.\text{NH}.\text{C}_6\text{H}_4.\text{COOH}$ ,

*Metaethylthiamidobenzoic acid*,  $\text{NHEt}.\text{CS}.\text{NH}.\text{C}_6\text{H}_4.\text{COOH}$ , melting at  $195^\circ$ ; and

*Metallylthiamidobenzoic acid*,  $\text{C}_3\text{H}_5.\text{NH}.\text{CS}.\text{NH}.\text{C}_6\text{H}_4.\text{COOH}$ , melting at  $189^\circ$ .

W. C. W.

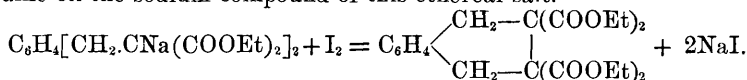
**Synthesis of Naphthalene Derivatives.** By A. BAEYER and W. H. PERKIN, junr. (*Ber.*, 17, 448—453).—The synthesis of tetrahydronaphthalenedicarboxylic acid ( $\beta\beta$ ) is accomplished by the action of orthoxylyl bromide on ethyl disodium acetylenetetracarboxylate.

For this purpose, the bromide (1 mol.) is dissolved in ether, 5 parts of alcohol are added, and the ether distilled off. Ethyl acetylenetetracarboxylate (1 mol.) dissolved in 5 parts of alcohol, and sodium (2 atoms) dissolved in 15 parts of alcohol, are added to the solution of the bromide, and the mixture is heated in sealed tubes at  $130^\circ$ . The product of the reaction is boiled with alcoholic potash, and after removing the alcohol by evaporation, the residue is dissolved in water, acidified, filtered, and the filtrate extracted with ether. The residue which is left on evaporating the ethereal extract is gradually heated to  $185^\circ$ , water and carbonic acid are given off, and the anhydride of tetrahydronaphthalenedicarboxylic acid remains as a crystalline mass, soluble in alcohol, ether, and chloroform. It melts at  $184^\circ$ , and

sublimes at a higher temperature. The anhydride is changed into the acid by solution in hot water and in alkalis. Tetrahydronaphthalenedicarboxylic acid,  $C_6H_4$   $\begin{matrix} \text{CH}_2-\text{CH.COOH} \\ | \\ \text{CH}_2-\text{CH.COOH} \end{matrix}$ , is freely soluble in

warm ether, chloroform, alcohol, and acetone, and less readily in hot water. It melts at  $199^\circ$  passing into the anhydride. The silver salt,  $C_{12}H_{10}Ag_2O_4$ , is thrown down as an amorphous precipitate, which gradually becomes crystalline. It is decomposed by heat into naphthalene and tetrahydronaphthalenedicarboxylic anhydride. The anhydride also yields naphthalene when its vapour is passed through a red hot tube.

*Ethyl orthoxylyldichlorodimalonic acid*,  $C_6H_4[CH_2.CCl(COOEt)_2]_2$ , is formed by the action of orthoxylyl bromide on an alcoholic solution of ethyl sodic chloromalonate at  $100^\circ$ . On reduction with zinc dust and acetic acid, the chlorine is displaced by hydrogen, and *ethyl orthoxylyldimalonate* is obtained. Ethylic tetrahydronaphthalenetetracarboxylate is produced by the action of an ethereal solution of iodine on the sodium-compound of this ethereal salt.



—On saponification, 2 mols. of carbonic anhydride are eliminated, and tetrahydronaphthalene-dicarboxylic acid melting at  $199^\circ$  is formed.

W. C. W.

**Acridine Picrate.** By R. ANSCHÜTZ (*Ber.*, **17**, 438—439).—*Acridine picrate* is a canary-coloured crystalline salt which begins to melt at  $208^\circ$ . It is insoluble in cold water, and is partially decomposed by boiling water. It is very sparingly soluble in benzene and alcohol. Chrysanine picrate is a brick-red powder, sparingly soluble in benzene.

W. C. W.

**Preparation of Quassin.** By ADRIAN and MOREAUX (*Pharm. J. Trans.* [3], **14**, 507—508).—The method recommended for the extraction, &c., of quassin yields a purer and more abundant product than the methods introduced by Wurtz, Wigger, &c.

Thin shavings of the wood are extracted with boiling water, potassium carbonate being added, 5 grams for every kilo. of quassia; the liquor is then concentrated to a magma, and exhausted with hot 90 per cent. alcohol. After 24 hours, the solution is decanted and treated with sulphuric acid diluted with 10 times its weight of 90° alcohol, until a precipitate forms, which is filtered off. The filtrate is treated with lime, 4 to 5 grams for every kilo. of wood, and after some hours the solution is removed from the solid matter by filtration, pressure, and washing with alcohol. The alkaline liquors are neutralised with carbonic anhydride, filtered, the alcohol distilled off, and the residue dried. In this way, a kilo. of quassia yields 8 grams of a friable substance, which is amorphous quassin. Crystalline quassin may be obtained by stopping the distillation of the alcohol before all the alcohol has volatilised, filtering, and allowing the remaining

spirit to evaporate slowly. The crystals may be purified by frequent recrystallisations and washing with 90° alcohol. The mother-liquors retain considerable quantities of both crystalline and amorphous quassin, which to a great extent can be regained by repeated agitation with chloroform. Crystalline quassin is white, light, soluble in chloroform, also in about 90 parts of cold absolute, or in 35 to 40 parts of 88° alcohol, scarcely soluble in ether; whilst 300 parts of hot water are required for its solution, from which it recrystallises on cooling. Amorphous quassin is nearly as bitter as the crystalline; it is readily soluble in absolute alcohol, and it is more soluble in ether and less so in water than the latter variety. D. A. L.

**Vesicating Principle of Croton-oil.** By H. SENIER (*Pharm. J. Trans.* [3], 14, 446).—In this paper, the conditions which affect the solution of English pressed croton-oil in alcohol and the composition and properties of the soluble portion are discussed.

It is observed that when croton-oil is mixed with equal volumes, or less, of alcohol (sp. gr. 0.794 to 0.800), a perfect solution is formed, which is permanent at ordinary temperatures. When, however, alcohol is added in larger quantities—for example, 7 of alcohol to 6 of croton-oil, or in still larger proportions, then part of the oil separates, the amount which separates varying in different samples. The dissolved oil is now soluble, whilst the separated oil is insoluble, in all proportions of alcohol. The insoluble oil is described in the Abstract (p. 947). The soluble oil (sp. gr. 0.987) at 60° F. is brown and holds in suspension acicular crystals, which dissolve on warming. It has an acid reaction, the characteristic croton-oil odour, a persistent burning taste, and produces pustules when applied to the skin. It is soluble in water, alcohol of various strengths, benzene, chloroform, ether, petroleum, &c.

Experiments were now made to determine the components or component of the vesicating principle. Various distillation experiments proved it to be neither a free volatile substance nor a combined volatile alkaloïd or alcohol. By saponification with sodium carbonate, it was shown not to be a free fatty acid; whilst a subsequent saponification of the neutral oils with sodium hydroxide showed it to be present amongst the combined non-volatile fatty acids. Several methods of separating the various acids were tried without success, and finally the following were adopted for separating these acids into groups:—Firstly, refrigerating the glycerides; those of the vesicating oils have the lowest solidifying point. Secondly, by the solution of the lead salts in ether and alcohol; the vesicating oil salt being soluble in ether, but insoluble, or nearly so, in alcohol. Thirdly, by fractional saponification; the vesicating oils being the least readily saponified. Fourthly, by fractional decomposition of the sodium salts; the vesicating principle being amongst the first acids liberated. In other experiments, after the successive removal of (1) acids having ammonia salts insoluble in alcohol (palmitic acid), (2) those precipitated by magnesium acetate from alcoholic solutions, (3) those having barium salts insoluble in alcohol; the vesicating substance was detected in those having (4) barium salts soluble in alcohol.

These latter acids, when separated, are dark brown and remain liquid at 50° F. From the various properties indicated, viz., low melting point of acid and glyceride, difficult saponification, solubility of lead salt, &c., it is assumed as probable that the new acid is allied to oleic acid, and its analogues ricinoleic and linoleic acids. The fatty acids of the neutral soluble croton-oil contain about 15 per cent. of (1), 20 per cent. of (2), 40 per cent. of (3), and 25 per cent. of (4). The free fatty acid, palmitic acid, constitutes about 22·5 per cent. of the soluble croton-oil.

D. A. L.

**A Crystallisable Colouring-matter in Chlorophyll.** By J. BORODIN (*Bied. Centr.*, 1884, 40—42).—In view of the unsatisfactory results obtained by the macrochemical or optical mode of investigation, the author has employed microchemical methods of investigation; the process is very simple. The green plants, which are the subjects of experiment, are digested with a little alcohol in the dark for about 24 hours, a drop of the fluid is then brought under the microscope, when a mixture of crystalline forms of different colours is seen; the observation is more satisfactory when a polariscope is used. The deep-green crystals formerly described by the author are formed and are easily distinguished by their colour and absence of double refraction; the behaviour of the various crystals with reagents is distinctive. Dilute sulphuric acid causes a green coloration, which is destroyed by ammonia or by merely washing with water; the dilution of the acid can be so managed that some of the crystals are coloured and others remain unaltered, pointing to a mixture of different colouring-matters. The behaviour towards solvents is confirmatory of this; certain red crystals dissolve easily in benzene, and sparingly in alcohol. There are violet crystals, but these are probably identical with the red viewed through a thinner medium. The crystals which dissolve readily in alcohol and sparingly in benzene are very different; they are of a yellow or brown colour, and are quickly attacked and dissolved by glacial acetic acid yielding a clear yellow fluid. Amongst the mass in the original fluid are scale-like forms of a straw-colour.

The plants which were the subject of experiment were *Spirogyra* and *Betula verrucosa*.

J. F.

**Orantin and Carottin.** By E. SCHMITT (*Bied. Centr.*, 1884, 215).—These two compounds are the principal constituents of annatto. The first is obtained by digesting 50 grams annatto with 100 grams sodium carbonate and 1 litre water, and evaporating to one-half. Carottin is prepared by digesting 125 grams annatto in  $\frac{1}{2}$  litre of oil.

E. W. P.

**Coal-tar Lutidine.** By O. DE CONINCK (*Compt. rend.*, 98, 235).—Coal-tar contains a lutidine identical with that one of the lutidines in Dippel's oil, which Ladenburg has lately synthesised, which he regards as a  $\gamma$ -ethylpyridine,  $C_8H_4NEt$ .

R. R.

**Some Reactions of Albumin.** By E. GRIMAUX (*Compt. rend.*, 98, 1336—1338).—When dilute solutions of albumin are mixed with



small quantities of sodium chloride, calcium sulphate, magnesium sulphate, ammonium chloride, &c., they become coagulable by the action of heat. In the case of albumin, as in that of the amidobenzoic colloid (p. 905), dilution with water neutralises the coagulating influence of salts. A similar effect is produced by passing carbonic anhydride into the solution. Albumin, as is well known, is not modified by dilution in the cold, but if the liquid is boiled, modification takes place. The author finds that if a 1 per cent. solution of albumin is heated at 90° for some minutes, the albumin undergoes complete modification. The limpid solution is not coagulated by boiling, but simply becomes opalescent. When treated with carbonic anhydride in the cold, it yields a gelatinous precipitate, which redissolves when a current of air is passed into the liquid. The precipitate also redissolves if the liquid is placed in a vacuum over potash, or if the precipitate is collected, washed, and placed in aerated water. Dilute acetic acid produces a gelatinous precipitate, easily soluble in excess, reprecipitated on neutralising with an alkali, but soluble in an excess of the latter. The addition of sodium phosphate prevents precipitation by carbonic anhydride, but not by acetic acid, and the solution gives all the reactions for casein. The modified albumin becomes coagulable by heat when the solution is mixed with small quantities of sodium chloride, calcium sulphate, &c. Carbonic anhydride does not completely precipitate solutions of modified albumin. The filtrate contains a peptone, and if the solution of albumin has been boiled for some hours instead of being heated at 80°, the substance precipitated by carbonic anhydride diminishes, and the amount of soluble peptone increases. It would seem that dilution dissociates albumin into free soda and an albuminoid which becomes hydrated and converted into an albuminate. With carbonic anhydride, this albuminate forms an unstable insoluble compound, which loses carbonic anhydride when exposed to air or in a vacuum, and redissolves. This last reaction is common to many colloids.

All the above reactions are obtained with the amidobenzoic colloid.

C. H. B.

**Metahæmoglobin.** By J. G. OTTO (*Bied. Centr.*, 1884, 212).—Metahæmoglobin contains as much oxygen as oxyhæmoglobin, only it is more firmly combined. The conversion of oxy- into meta-hæmoglobin is a change from a loose molecular into a chemical combination.

E. W. P.

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### Physiological Chemistry.

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**Respiration in a Superoxygenated Atmosphere.** By L. DE ST. MARTIN (*Compt. rend.*, **98**, 241—243).—The paper describes experiments on the products of the respiration of animals in a super-

oxygenated atmosphere; the result being that the chemical phenomena are found to undergo no sensible change. R. R.

**Experiments on Digestion.** By M. OGATA and others (*Bied. Centr.*, 1884, 18—20).—The author reports experiments on digestion when the inner coating of the stomach had been removed, and he finds that the glands of the large intestine are capable of carrying on the process of digestion of flesh, raw and cooked eggs, and other albuminous foods, which, when divided into small portions, are easily decomposed by the secretions. Edinger concludes from his investigations that acid reaction does not take place in the intestine, but on the surface of the stomach. Falk has investigated the action of the digestive fluids on ferments. Yeast is not injured in its action by trypsin or decomposing infusion of pancreas, but it is by bile, which precipitates the invertin, at least after standing some hours. The influence of saliva and gastric juice could not be determined, as both secretions invert cane-sugar. Alcoholic fermentation is not hindered by saliva, pancreatic fluid, or bile; gastric juice and hydrochloric acid of equal concentration prevent it; bacteria destroy yeast in a short time. Zawarykin contributes to the knowledge of absorption of fat in the intestines of animals. He has observed that the lymph cells take up the fatty particles by a sort of amoeboid movement, raising and lowering themselves in alternate regular motions; the fat is then directly absorbed into the venous blood. Voigt has made extensive experiments on the functions of the bile in taking up nourishment from the intestinal canal. He says that in the digestion and absorption of albumin in the form of flesh, the bile does not play an important part. Glucose or bread, when eaten with meat, does not affect the absorption. On the contrary, bile plays a most important part in the absorption of fat. The antiseptic properties of bile have not been proved, and the food taken does not appear to influence the composition of the bile; but the dry matter contained in it depends greatly on the amount of nourishment taken.

J. F.

**Formation of Fibrin.** By J. HLAVA (*Bied. Centr.*, 1884, 212).—Fibrin is formed by the death of the white blood-corpuscles, and is at first granular, afterwards more consolidated; the fibrin ferment does not exist in the protoplasm of the corpuscles. E. W. P.

**Formation of Fat from Carbohydrates in Animals.** By N. TSCHIRWINSKY and others (*Bied. Centr.*, 1884, 9—16).—The subjects of experiment were two young pigs from the same litter, similar live-weight, and brought up under the same conditions. At the commencement of the experiment, one of the animals was slaughtered, and the quantity of substances found taken to represent the composition of the living animal: two series of experiments were made under these conditions. The one pig was killed and analysed on 10th December, the other was fed on barley until 10th April following; the food contained altogether 9526.59 grams nitrogenous matter, and 1114.43 grams of fat: three estimations were made during that time of the amount actually digested, and it was reckoned that the quantity

was 7493·87 grams nitrogenous matter, and 655·56 grams fat. The animal was then killed, and immediately examined.

The body was found to contain—

	Nitrogenous compounds.	Fat.
	2516·92 grams	9264·18
From which deduct, found in animal killed at commencement of experiment . . . . .	957·47 „	687·58
Leaving . . . . .	1559·45 „	8576·60

as deposited from 10th December to 10th April; assuming that the fat contained in the food and digested was directly assimilated, there remains to be accounted for 7921 grams of newly formed fat. The albuminous matter present was not sufficient to form this quantity; if from the total amount digested the amount formed, 1559·45 grams, be subtracted, the remainder, 5935 grams, would only produce at the rate of 51·4 per cent. a maximum of 3051 grams of fat, leaving a considerable balance to be accounted for.

A second experiment carried out in a similar manner gave similar results. The nitrogenous matter and fat digested were far from sufficient to account for the amount of fat found in the carcase. Both experiments show that the carbohydrates take part in the formation of fat.

The experiments of Meissl and Strohmer were also made on swine, but a different course was taken, the total amount of nitrogenous matter and fat in the food given being estimated, also the amounts excreted in the excrement, urine, and respiration products. The animal was kept in a peculiarly constructed moveable stall arranged so that the excrement and urine were separately collected: in close proximity was a respiration apparatus on Pettenkofer's system. The experiment lasted for seven days; barley meal and rice were employed as fodder; the result *per day* in grams is given—

Carbon.			Nitrogen.		
Consumed.	Excreted.	Assimilated.	Consumed.	Excreted.	Assimilated.
grams.	grams.	grams.	grams.	grams.	grams.
756·37	476·15	289·22	18·67	12·59	6·08

The calculations of the authors show the fat to be derived from three sources: from the food, 7·9 grams; from nitrogenous matter in the body, 33·6 grams; from carbohydrates, 310·3 grams per day, and their opinion is that generally seven to eight times as much fat is derived from the carbohydrates as from all other sources.

J. F.

**Proportion of Incompletely Oxidised Phosphorus contained in the Urine.** By R. LEPINE, EYMONNET, and AUBERT (*Compt. rend.*, 98, 238—241).—In the urine of patients suffering from apoplexy, epilepsy, delirium tremens, fatty degeneration of the liver, and certain other diseases, the authors have found a greatly increased proportion

(as compared with the nitrogen) of incompletely oxidised phosphorus, that is, not in the state of phosphates. R. R.

**Physiology of the Formation of Milk.** By H. THIERFELDER (*Bied. Centr.*, 1884, 174).—From experiments which he has made, the author believes that lactose is produced in the animal from blood serum through the medium of a ferment which he terms *saccharogen*, but he has not isolated this substance, yet considers it to be soluble in water, insoluble in alcohol and ether, decomposed by boiling, and not identical with glycogen. Casein is most probably formed from serum-albumin by an analogous ferment present in the lactic glands.

E. W. P.

**Diseases of Animals.** By ROLOFF and others (*Bied. Centr.*, 1884, 29—32).—Inoculation against splenic fever with Pasteur's protective lymph is declared to be safe, but a sufficient quantity must be used and certain precautions taken. The increase of the bacterium of this fever is known to take place by division, but sometimes by spores, and both processes are carried on in the organism during the state of fever. The blood of animals in the disease does not contain bacilli until a short time before death, at least 10 hours, and the blood before they appear does not convey the disease if injected into a sound animal.

The author thinks that the bodies of animals even in a healthy state contain the bacteria of splenic fever, but in a third state, dormant, and seeks to identify them with the shining corpuscles of Archangelski, which he thinks are spores.

Gibier contributes notes on the subject of hydrophobia; the disease appears the sooner after the bite the nearer that is to the brain; particles of brain substance convey the disease by inoculation. The disease is also hereditary; rabbits in young inoculated two days before parturition gave it to their young who died of it, and matter from their brains communicated the disease to others. Cold diminishes the effect of the poison; at  $-25^{\circ}$  it commences to diminish; at  $-35^{\circ}$  the action is doubtful; at  $-40^{\circ}$  it ceases. In the brain and spinal marrow of animals which have died of the disease, Gibier found small spherical organisms, two of them sometimes united by a long hair-like thread, and others single, bearing a short hair-like appendage, probably a portion of the line which had previously united two of them.

Israël and Wassilieff have made some experiments with the bacilli of glanders. The former cultivated two kinds of fungi from the lungs of a horse dead of the disease; one was active and communicated the disease to rabbits, the other inactive. Wassilieff found in the blood of a postillion who died of glanders, thread-like bacteria similar in size to those of tuberculosis, and containing two to four spores: he also found them in the nasal discharges and the pustules.

J. F.

**Irritant Properties of Oats.** By SANSON (*Bied. Centr.*, 1884, 20—21).—Experiments made at the agricultural school of Grignon show that oats contain a matter easily soluble in alcohol, which has an irritant action on the motor cells of the nervous system. It is not

vanillin, but a nitrogenous substance apparently of an alkaloidal character, uncrystallisable, granular, and of a brown colour. Its composition is given as  $C_{56}H_{21}NO_{18}$ , and is called by the author *avenin*. The quantity present varies according to the quality of the grain and soil on which it is grown. The darker varieties contain more than the lighter coloured. When the quantity in air-dried grain does not exceed 0.9 per cent., the irritating action is slight, but beyond that amount it becomes strong. The bruising and milling of oats diminishes the quantity of substance materially, but it is quicker in its action. After the administration of 1 kilo. of oats, the irritation of the motor nerves lasts an hour, gradually increasing to a maximum and diminishing. The importance of the subject to owners of horses lies in the advantage of feeding with grain in the natural state. J. F.

**Poisonous Matter of Lupines.** By ARNOLD and SCHNEIDEMÜHLE (*Bied. Centr.*, 1884, 32—34).—The preparation of the extract is described—2 to 5 grams are sufficient to kill a dog—the poisonous properties are increased by the presence of alkalis in the solution, diminished by that of acids; the organ first attacked is the liver. The blood vessels appear to convey the poison, as fatal effects rapidly follow hypodermic injection or injection into a blood vessel: the fatal effects of eating lupines are probably caused by wounds in the alimentary or digestive organs. Allowing the poison direct access to the blood, after repeated doses gradually increased, animals gain a certain amount of immunity, and can withstand large quantities. As a cure, acid drinks, plenty of clean cold water, and purges of Epsom salts are recommended. J. F.

**Behaviour of "Folia Uvæ Ursi" and Arbutin in the Animal Organism.** By L. LEWIN (*Pharm. J.* [3], 14, 490).—From recent investigations it is shown that the therapeutic value of *Uva ursi* (bear-berry) leaves is due to the quinol (arbutin) they contain; the tannin simply exerting a very slight auxiliary action. From experiments with arbutin, it is observed to split up in the body, in the same way as it does outside it, namely, into sugar and quinol; the whole quantity taken into the system, however, is not decomposed; therefore quinol and also some unchanged arbutin are found in the urine, which on even brief exposure to the air undergoes change of colour, becoming olive-green or brownish, at the same time gradually losing its acidity, until it finally becomes alkaline. These changes are due to oxidation; when the urine becomes alkaline in the bladder, these changes take place inside, and the urine is voided of an olive-green colour. Exactly similar changes take place in human urine after treatment with *Uva ursi* leaves, and hence arises the fact stated above with regard to these leaves. Quinol acts as an antizymotic and antiseptic even in a 1 per cent. solution; urine containing it remains undecomposed for two weeks even when exposed to the air; other urine not containing it undergoes speedy decomposition. Moreover, the dark oxidation-products of quinol act as irritants, and these are beneficial in catarrhal affections of the mucous membrane, making

them turgid, and starting reparative action. It is these properties of quinol which make it, and also the *Uva ursi* leaves, of therapeutic value. In conclusion, the author suggests that larger doses than are now given should be administered when *Uva ursi* leaves are used; employing from 30 to 80 grams in 180 of menstruum, removing tannin by agitation with charcoal and filtration.

Or a still greater improvement would be to use arbutin instead of the leaves, making powders with 1.0 gram arbutin and 0.5 gram sugar, or dissolving in water. It may be given hypodermically. Clinical experiments show that arbutin is a valuable therapeutic agent; it is not poisonous and in splitting up does not set free in the body sufficient quinol to exert poisonous action. Arbutin is lævrotatory.

D. A. L.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Effects of Light on the Respiration of Oxygen by Plants.** By J. REINKE (*Bied. Centr.*, 1884, 37—39).—This paper is an examination of Pringsheim's theory (*Abstr.*, 1880, 560), and the author's experiments were limited to the observation of the amount of gas exhaled during varying amounts of sunshine: the evolution of gas begins when the light is fairly strong, and increases as the light becomes more intense, until the maximum is reached. This corresponds with the moment of direct sunlight; further intensification of light prolongs the evolution of gas, but does not increase its rapidity; and when the rays are concentrated by a lens, the process proceeds in this way until the chlorophyll is destroyed. J. F.

**Influence of Constant Temperatures in the Soil on Plants.** By HELLRIEGEL (*Bied. Centr.*, 1884, 179—190).—The plants were grown in artificial soil composed of sand, to which were added 136.1 mgrms. potassium hydrogen phosphate, 149.2 mgrms. potassium chloride, 24 mgrms. magnesium sulphate, 410 mgrms. calcium nitrate, and 1.6 mgrms. ferric chloride, and placed in glass vessels 26 cm. high and 8 cm. broad, and it was so arranged that the mixture could be kept at a definite temperature, and have always 150 grams water per kilo. sand. It was found that when the temperature remained at 40°, that barley plant roots did not develop themselves; that a temperature of 30° was not fatal to barley, but still the plant did not thrive; that at 20° the results were best; and at 10° certain abnormal results, such as very strong roots of the first and second order, the latter being very short and warty, were observed, but yet no definite damage could be noticed. When other plants were experimented with, such as rye and wheat, it was noticed that a low temperature produced stronger stems and leaves, whilst a high temperature, as it caused the growth to be rapid, produced stems and leaves thinner and weaker. Wheat, for its energetic



growth, required a higher temperature than rye; and the assimilation during the young life of rye was most energetic at 20°, barley at 25°, and wheat at 30°. It is also shown that to produce strong growth with fully formed seeds, the period of maximum intensity of light and heat must coincide with that of the maximum period of leaf formation; consequently it should be so arranged that the time of seeding should occur about the end of July. E. W. P.

**Influence of Solar Rays on the Temperature of Trees.** By E. IHNE (*Bied. Centr.*, 1884, 63).—The author inserted thermometers at different depths into the trunk of a maple tree, also in a branch and twig. He found that in a fine clear day the variations of temperature were not large, the exterior layers were higher than the interior, and the sections of larger diameter were the warmer; but on the whole the variations were slight, and the temperature at all times of observation a considerable number of degrees above that of the surrounding atmosphere. J. F.

**Formation of Starch-transforming Ferments in the Cells of Highly Organised Plants.** By W. DETMER (*Bied. Centr.*, 1884, 69—70).—The experiments recorded were intended to ascertain the influence of atmospheric oxygen on the formation of these ferments.

Seeds and seedlings of *Triticum vulgare* were the subjects of experiment; portions of both were grown in ordinary air, part in an atmosphere of hydrogen. They were then pounded and extracted with water; the solutions obtained from the air-grown plants and grains showed a very much more powerful diastatic effect than those grown in hydrogen, the conclusion arrived at being that the presence of oxygen is a necessary condition of the development of the ferment. J. F.

**Lime and Magnesia in Plants.** By E. v. RAUMER (*Bied. Centr.*, 1884, 46—48).—Observations on plants of *Phaseolus multiflorus* show that the functions of lime are connected with the building up of the tissues and the formation of the cell-walls, but is not concerned in the formation or transformation of starch. The office of magnesia, on the contrary, is to assist in the starch-forming process, and the development of chlorophyll. Magnesia is always present in the latter, and its presence is necessary to healthy growth and colour. J. F.

**Experiments with *Drosera Rotundifolia*.** By H. BÜSGEN (*Bied. Centr.*, 1884, 47—49).—The author mentions previous experiments intended to answer the question whether the capture of insects by these and similar plants assists their development. Kellermann, v. Raumer, Rees, and F. Darwin are for the affirmative, but Regel denies that there is any useful effect. The author thinks the difference of opinion is due to the various experiments being made under different conditions, and with plants possibly in different stages of development. To carry out comparative experiments in a trustworthy way, the comparison should commence with the weighing of the seeds and finish with the estimation of the total dry matter of the plant. The seeds of *drosera* are so extremely minute that they may be

left out of account, and the author commenced with the seedlings—they were grown in peats, previously boiled in a nutritive solution; these were placed on saucers and covered with bell glasses; one set were fed with the lice from vine leaves, the other received no such nourishment. The unfed plants were less strong and healthy than the other; the fed plants had 17 flower branches on 14 plants against 9 buds on 16 unfed; 90 seed capsules on 14 plants, against 20 on the 16; the last doubt was cleared up when the total dry weight was taken, the fed plants weighing 0.352, the unfed only 0.119 grams; other trials under less favourable conditions gave similar results, and the author considers it as proved that the plants of *drosera* are capable of utilising animal food and assimilating it beneficially for the production of seeds. J. F.

**Withering of Flowers and Leaves.** By J. WIESNER (*Bied. Centr.*, 1884, 43—44).—In most plants, the leaves transpire moisture in larger quantities than the flowers; and, as a rule, cut flowers wither more slowly than leaf twigs. If the transpiration of the leaves is arrested, the flower will remain a long time fresh as when severed, so that it would seem the flowers are deprived of moisture by the leaves. In like manner growing plants, when insufficiently supplied with moisture, either bloom slowly or not at all. This action of the leaves explains why in cut twigs the terminal sprout withers even when plunged under water, and why this terminal leaf-bud lasts longer on twigs deprived of their leaves than when they are left on. J. F.

**Easily Oxidisable Substances in Plant Sap.** By C. KRAUS (*Bied. Centr.*, 1884, 45—46).—The author describes experiments made on the sap contained in the tubers of *Dahlia variabilis*, which he cut into slices. The surfaces gradually became yellow, and with longer time penetrated below the surface; the bulbs swelled, turning green in the light, and pale green chlorophyll bodies appeared. The yellow tinged cells contained a yellow or reddish sap: the surfaces of the slices were not only yellow but showed red points and streaks, whilst in the interior of the cells there was a red colouring matter turned green by alkalis. The author thinks the change of colour is due to oxidation. J. F.

**Notes on the Bean of Soja Hispida.** By E. MEISSEL and F. BÖCKER (*Bied. Centr.*, 1884, 52—53).—The soja bean contains no proteid matter in the form of gluten, and very little in the form of amides; the albumin, soluble in water or 10 per cent. potash solution, resembles the legumin of leguminous fruits in its behaviour towards reagents, and is put down as casein by the author, or possibly a modification thereof; its ash-free composition is C 52.58, H 7.00, N 17.27 per cent. The matter soluble in ether consists of 90 per cent. neutral fat, and 5—10 chlolesterin and other similar substances. In the remaining non-nitrogenous matter, besides cellulose, is found some sugar equal to 10 per cent. dextrin, and less than 5 per cent. starch, in the form of small spherical grains; in round numbers the composition of the bean is: Water 10, soluble casein 30, albumin 0.5, insol-

ble casein 7, fat 18, cholesterin, &c., 2, dextrin 10, starch 5, cellulose 5, ash 5, traces of sugar and amido-compound. J. F.

**Natural and Renewed Succirubra Bark.** By J. HODGKIN (*Pharm. J. Trans.* [3], 14, 481).—The author publishes the results of the analysis of samples from the same consignment of bark; of quills of entirely natural bark (1), entirely renewed bark (2), and also of quills of natural and renewed bark in juxtaposition; the upper half being renewed bark (3), and lower natural (4). Bark (2) contained largest amount of total alkaloids and quinine, the others being in the following order: (3), (1), and (4). (3) and (4) contained much moisture, 15·96 and 14·61 per cent. respectively. The natural bark (4) seems to have suffered in renewal, which is probably due to injury to the tree caused by the shaving process, which it is suggested was evidently employed in this case. D. A. L.

**Seeds of *Bassia Longifolia* and the Fat contained therein.** By E. VALENTA (*Dingl. polyt. J.*, 251, 461—465).—The seeds of this tree are 1 to 2 cm. long, and enclosed in a brown skin. They have a peculiar odour and bitter aromatic taste. 100 parts of the seeds dried at 100° gave—

Fat (light petroleum extract).....	51·14
Soluble in absolute alcohol .....	7·83
Tannin .....	2·12
Bitter principle soluble in water.....	0·60
Starch.....	0·07
Vegetable mucilage .....	1·65
Albuminous substances soluble in water ..	3·60
Extractive substances soluble in water....	15·59
Insoluble proteids.....	4·40
Total ash .....	2·71
Fibre and loss .....	10·29

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Ash in the soluble portion.....	0·95 per cent.
Total proteids.....	8·00 „

For the extraction of the fat, light petroleum boiling at 40—45° was used. The fat has a yellow colour and greasy consistency; but on exposure to the air and light the colour disappears, and the fat soon becomes rancid. It has a sp. gr. of 0·9175 at 15°, melts at 25·3°, solidifies at 17·5—18·5°. It contains considerable quantities of free fatty acids, but only a small amount of glycerol. 1 gram of the fat requires 192·3 mgrms. KHO for the complete saponification of the fatty acids. It is partly soluble in alcohol, and perfectly soluble in ether, carbon bisulphide, benzene, &c. The fatty acids obtained by saponifying the fat with potash-ley, and decomposing the resulting soap by means of a 10 per cent. solution of hydrochloric acid, have a white colour, and pleasant odour and taste. They melt at 39·5°, solidify at 38°, and dissolve readily in alcohol.

According to Schädler, Makwah butter consists of 80 per cent.

stearin and 20 per cent. olein; the author, however, found that it contained palmitin and olein.

The ash of the seeds is yellowish-white and dissolves almost completely in water. It gives by analysis—

Silicic acid and portion insoluble in nitric acid . . . .	10·67
Phosphoric acid. . . . .	15·47
Sulphuric „ . . . . .	6·81
Carbonic anhydride . . . . .	7·46
Ferric oxide and alumina. . . . .	2·01
Lime . . . . .	0·64
Potash and soda (the latter is present only in traces)	56·68
Moisture and loss . . . . .	0·26
	D. B.

**Suggestions for the Destruction of Phylloxera.** By BALBIANI and others (*Bied. Centr.*, 1884, 49—52).—The treatment of vine stems by coal-tar in order to destroy the winter eggs is not found either to injure the growth or impart a disagreeable flavour to the grapes. Lafitte gives statistics which show that the replanting of the injured vineyards is being chiefly carried on with French rather than American vines. Mouillefert gives instructions for the employment of potassium thiocarbonate as an insecticide. He recommends 1 part of the salt to 333 or up to 400 of water; this solution is very effective and destroys the eggs. He says, moreover, that it is the degree of dilution which is of importance in using this substance: as much as a kilogram may be applied to a vine, provided the solution is not stronger than he advises; while 50 grams in concentrated solution would infallibly kill the strongest vine. He recommends plentiful use of pure water after the insecticide has penetrated the soil, and that in the South of France the treatment should be carried out twice in winter from November to April, and again in June or July. Servantie also commends the use of the thiocarbonate as a most useful agent, capable of being used without danger at all seasons of the year, but it must be a pure compound, containing more than 12 per cent. carbon bisulphide, and more than 18 per cent. potash. Contradictory opinions as to the value of pyridine are given, but its high price is against its use. Other experiments, the injection of fluids into the vine-sap are mentioned, but the results are uncertain.

J. F.

**American Red Clover.** By HARTZ and others (*Bied. Centr.*, 1884, 53—54).—During seasons when native red clover-seed is scarce, the use of American seed is advised, provided it is from Canada, the climate of which resembles that of Steiermark and Tyrol, and seeds produced there should be easily acclimatised. The price of American seed being lower than that of European, experiments were made as to the produce of both, in which the quantity and quality of hay produced was considerably in favour of the higher-priced European. The two kinds are distinguished by the American plant being covered with protruding hairs, whilst on the other the hairs lie flat on the leaves.

J. F.

**Cultivation of Sorghum Halepense.** By V. BARATTA (*Bied. Centr.*, 1884, 56—57).—Reports of unsuccessful attempts to cultivate this plant in different parts of Austria. In only one case out of four were seeds produced, and an experimenter complains that the very large spreading roots rendered the after culture very difficult. J. F.

**Diffusion Residues as Cattle Food.** By M. MÄRCKER (*Bied. Centr.*, 1884, 21—28).—The author continues his investigations on the value of these residues (see Abstr., 1883, 695). He has previously shown that the usual mode of storage causes a loss of one-third of the substance, and recommends drying before storing. The present paper is a record of a number of feeding experiments on milch cows, oxen, horses, sheep, and swine. The cows, oxen, and sheep eat it readily, with excellent results. Horses refuse it; swine take to it badly and waste it. The dried substance keeps as well, and is as little hygroscopic as other dry fodders. It can be used as a substitute for a certain quantity of hay, and the milk of cows is not affected injuriously, but the process of fattening is somewhat slower than when animals are fed on hay. J. F.

**Sugar-beet Culture and Manuring.** By NOWOCZEK (*Bied. Centr.*, 1884, 34—37).—This a report of extensive trials of various kinds of sugar-beet. Certain varieties are recommended: the chief point of interest is the beneficial effect of artificial manures on the yield of sugar in the juice. J. F.

**Cultivation of Winter Flax.** By A. LEYDHECKER (*Bied. Centr.*, 1884, 55—56).—The author tried the culture of this plant in Northern Bohemia, where the summer variety had hitherto been alone cultivated with good results, and found the loss in steeping, hackling, and other processes but little more than with the early species. He recommends its cultivation. J. F.

**Analysis of Soils.** By G. LECHARTIER (*Compt. rend.*, 98, 1339—1342).—When a soil is boiled with a solution of ammonium oxalate containing an excess of ammonia, some of the organic matter and a certain proportion of the inorganic constituents, *i.e.*, phosphoric acid, ferric oxide, alumina, &c., pass into solution. Ammonium citrate exerts the same solvent power, but dissolves some of the calcium existing as carbonate; whereas the ammonium oxalate dissolves only the calcium in combination with the organic matter. The tartrate has less solvent power, except in the case of calcium. Ammonium chloride dissolves a part of the humous substances and some of the inorganic constituents, but has little action on the phosphates. It may be used, however, to dissolve out the calcium existing naturally as carbonate, and that added in manures. The solvent action of these substances varies with the strength of the solution, the presence or absence of an excess of ammonia, and the length of time the liquid is kept in ebullition. If the organic matter is destroyed by roasting the soil at a low temperature, the proportion of phosphoric acid and

potassium which dissolve in ammonium oxalate, is not altered, but the proportion of ferric oxide and silica, which becomes insoluble, is much higher than that existing in the decomposed organic matter.

In actual analysis, 20 grams of the dried soil are placed in a flask with 250 c.c. of a solution containing 10 grams of ammonium oxalate and an excess of ammonia; the flask is connected with an inverted condenser, and the liquid boiled for several hours. It is then filtered, evaporated to dryness, the solid matter ignited, the residue treated with hydrochloric acid, and the various substances estimated in the solution.

C. H. B.

**Influence of a Crop and Shelter on the Physical Properties of a Soil.** By E. WOLLNY (*Bied. Centr.*, 1884, 152—160).—Various soils, peat, quartz, loam and chalky sand, were experimented on as regards their temperature when left exposed, covered by straw, or by grass. It was found that during the warm season the bare soil was much warmer than the sheltered, and the soil sheltered by manure (straw) warmer than that covered by grass. At the hour of the daily maximum of the terrestrial temperature, the difference between the temperatures of the shaded and exposed soil is greatest, whilst at the minimum temperature the exposed is generally cooler than the sheltered soil. The daily variations are greater in the exposed than in the sheltered soil, and less in the grass-grown than straw-covered soil. The influence of the coverings on the temperature is so great that it almost completely negatives the specific relations of the several soils themselves towards radiant heat. When soil is covered by vegetation or by dead vegetable matter, as stubble or manure, it is considerably warmer in summer at some distance below the surface, and colder in winter than a fallow; but should a warm period in winter or a cold in summer intervene, then the influence of the covering makes itself felt in the opposite direction. Experiments with quartz sand show that the bare soil is more rapidly warmed by the sun than the covered soil; consequently, in spring it is more quickly heated, and in autumn more rapidly cooled. When land is covered by a crop, the crop exerts a very decided influence on its temperature, dependent on the thickness of sowing, the age of the crop and its character, but when the conditions are similar, then the effects on the temperature are similar; but whether the plant itself has influence is uncertain. But when we come to the method of planting, a difference is found, for the thicker the sowing and the stronger the plant, so is the temperature during the warm season lower and the variations less. Soils warm more rapidly when the crop is sown by a drill than when broadcast; an advantage is gained also, when the drills are wider apart and run north and south. With perennials, the temperature rises after mowing. It appears that there is a considerable loss of heat by radiation from a field of, say clover, for below the surface of the crop the temperature is lower than the surface of a fallow. This reduction is due to radiation from the plants themselves, but its effects are considerably counteracted by the absence of radiation from the soil.

E. W. P.

**Thermal Conductivity of Soils.** By F. WAGNER (*Bied. Centr.*, 1884, 145—152).—The research on the thermal conductivity of the soil constituents was commenced, because it was thought that E. Pott's results (*Landw. Versuchs.-Stat.*, 1877, 273) were incorrect, as he did not use pure materials. The apparatus which the author has employed consists of an india-rubber cylinder 32.5 cm.  $\times$  10 cm., the heat being communicated by a copper cylinder 12 cm.  $\times$  12 cm. placed at right angles to it. Into the india-rubber tube are inserted six thermometers at a distance of 6 cm. from each other, the first being 1 cm. from the commencement of the tube. With dry soils a heat of 70° over the original temperature was employed, but with moist soils a temperature of 35° only. The soils experimented on were washed quartz powder, pure kaolin, precipitated chalk, ferric hydroxide, a peat purified by hydrochloric acid, alcohol, and ether (this contained 8.05 per cent. ash and 3.54 volume per cent. moisture); also humus produced from sugar by the action of sulphuric acid, containing 0.79 per cent. ash and 1.54 per cent. moisture. When the materials lay closely together, the order, as determined by their relative conductivities, was as follows: peat, sugar-humus, kaolin, chalk, ferric hydroxide, and quartz, the mean difference between the thermometers being in the first soil 4.56, in the last 5.66. But when those soils were loosely packed in, the order is altered; chalk, kaolin, ferric hydroxide, sugar-humus, peat, and quartz; thermometric differences, chalk 4.34°, quartz 5.11°. It would be impossible to give a full account of the other experiments which were made with natural soils without introducing various tables of figures, but the chief results may be summed up as follows: the conductivity of any one soil is increased by the closeness of its particles, and it is also raised by increasing quantities of moisture. As a rule, the conductivity in a dry soil increases with the increased size of its particles; finally, the presence of water generally in a soil assists the transmission of heat.

E. W. P.

### **Morphology and Chemistry of Natural and Artificial Ulmin.**

By J. J. FRÜH (*Bied. Centr.*, 1884, 3—9).—Microscopic preparations of different kinds of turf show two regularly-recurring typical forms, which are similar in colour and transparency, a pale rusty running to a clear yellow, something like softened gutta-percha. One is granular, consists of well-formed spherical and oval grains, mixing readily with water, and easily soluble in 5 per cent. potash solution; the second is the homogeneous form, which the author believes to be derived from the first. It exists in homogeneous plates or layers, and contains various vegetable cells. He thinks this the highest form of ulmin in peat. He then describes the process by which Sestini obtained saculmic acid and saculmin (*Abstr.*, 1880, 865, and 1882, 605), and thinks the natural and artificial products are identical. He traces the similar behaviour of both with reagents, especially towards the 5 per cent. potash solution, in which the granular forms of both contract, and assume the homogeneous form. The author thinks it probable that there are two groups, ulmin and humin, distinguishable from each other with great difficulty. Dopplerite is a modification of ulmin

combinations (Abstr., 1883, 160, 427), the formation of dopplerite is described, so-called stone-turf being the intermediate form; the presence of much water and little air are favourable to its production. Dopplerite is not to be confounded with the pitch and shining coal found and described by Zincken. J. F.

**Comparative Nitrifying Effect of Various Salts.** By PICHARD (*Compt. rend.*, **98**, 1289—1290).—In barren soils consisting almost entirely of sand, the nitrogen of organic matter is not converted into nitrates unless a small quantity of nitrifying earth be added. Potassium, sodium, and calcium sulphates, in the proportion of 0·5 per cent., exert an energetic nitrifying action, the effect being especially marked in the case of the calcium sulphate, probably on account of its comparative insolubility. Other things being equal, nitrification is more complete in a fine-grained than in a coarse-grained soil, because of the more regular aëration and moistening of the former. The nitrifying power of equal weights of different salts, that of calcium sulphate being 100, is as follows:—

Calcium sulphate.....	100·00
Sodium „ .....	47·91
Potassium „ .....	35·78
Calcium carbonate.....	13·32
Magnesium „ .....	12·52

These ratios may vary with the strength of the solutions in the case of potassium and sodium sulphates, but in the other cases they may be regarded as constant. Under the climate of Central France, nitrification in calcareous soils or in soils which have been treated with calcium sulphate, is very active in September and October. During this time, the proportion of nitric nitrogen to total nitrogen rose to 26·15 per cent. in a soil to which calcium carbonate had been added, and to 46·29 per cent. in a soil which had been treated with calcium sulphate. The nitrifying power of potassium sulphate explains the success which attends its application to tobacco, and the similar but much greater power of calcium sulphate accounts for its beneficial action on lucerne, to which it is applied in the form of plaster of Paris, or of superphosphate rich in calcium sulphate.

The application of plaster of Paris in the proportion of 0·5 to 1 per cent. to soils poor in calcium compounds cannot be too highly recommended, and its effect will be especially marked on clay soils, which do not allow the infiltration of the nitrates. If the presence of calcium sulphate does not confer fertility on soils naturally rich in gypsum, it is because they almost always contain chlorides of the alkalis and alkaline earths, especially sodium chloride, which are well known to be detrimental to nitrification. C. H. B.

**Stable Manure.** By P. P. DEHÉRAIN (*Compt. rend.*, **98**, 377—380).—From the experiments described in the paper, it is inferred that the high temperatures observed in manure are due to the oxidation of organic matter by free oxygen; moreover, this oxidation is only partially induced by a definite ferment (bacilli), whilst the dis-



engagement of marsh-gas in manure deprived of oxygen is exclusively due to the action of the ferment. R. R.

**Analysis of Peat Litter.** By M. FLEISCHER (*Bied. Centr.*, 1884, 210).—Analyses of three samples of peat litter after use are given; although the samples were moist, they were not sufficiently so to prevent carriage: nitrogen, potash, and phosphoric acid varied considerably. E. W. P.

**Manuring Barley and Oats with Nitrogen and Phosphates.** By M. MÄRCKER (*Bied. Centr.*, 1884, 162—166).—Pott has previously stated that in Saxony, farmyard manure is not of much value for barley, nor is kainite. The author has applied to barley after sugar-beet 150 kilos. Chili saltpetre per hectare, and to oats 200 kilos.; these crops were grown in at least 20 different districts, the character of the soil varying from sandy to heavy.

It was found that on the average the yield of barley was raised only 7·5 per cent., whilst that of the oats was increased 31·7 per cent.; but as regards the straw, the increase was nearly equal, showing that the nitrogenous manuring exercises a more intense action on the formation of grain in the oat than in the barley plant. In another set of experiments, 40 kilos. of superphosphate were added to the Chili saltpetre, with the result that the yield of barley was very largely increased, whilst though the yield of oats was raised, yet it was only to a small extent: the same may be said for the straw. The analyses of the ash of both plants does not explain the advantage of employing phosphate, but the higher yield is probably due to a deeper ramification of the roots, whereby a better use can be made of the materials present. E. W. P.

**Manurial Value of the Lime-waste of Sugar Factories.** By F. STROHMER (*Bied. Centr.*, 1884, 210).—Water 33 per cent.,  $\text{CaCO}_3$  57, other mineral matter 1 per cent., including 0·8 per cent.  $\text{P}_2\text{O}_5$ , organic matter 9 per cent. (0·3 per cent. N). E. W. P.

**Use of Superphosphates.** By P. P. DEHÉRAIN (*Compt. rend.*, 98, 1286—1289).—A mere determination of the total amount of phosphoric acid in a soil is of little value as a guide to the use of superphosphate. It is necessary to ascertain whether the phosphates are soluble in carbonic acid (calcium and other protoxides), and therefore assimilable by plants, or insoluble in carbonic acid (iron and other sesquioxides), and therefore non-assimilable. For analytical purposes, carbonic acid may be replaced by acetic acid. In comparing the amount of phosphoric acid in different soils, the depth of the latter should be ascertained, and the phosphoric acid stated at so much per superficial area. From the results of recent experiments by different chemists, it would seem that when the total amount of phosphoric acid is more than 4000 kilos. per hectare, a portion being soluble in acetic acid, and the land is treated regularly with farmyard manure, the use of superphosphates is unnecessary. This supposition, however, requires confirmation. C. H. B.

**Manuring with Crude Ammonium Superphosphate.** By E. WOLLNY (*Bied. Centr.*, 1884, 167—170).—When superphosphate is exposed to coal-gas containing ammonia, but freed from tar, a certain amount of ammonia is absorbed, and a “crude ammonium superphosphate” containing 7.5 per cent. of ammonia is produced; but at the same time a certain quantity of thiocyanate is also retained, and it was thought that this might be injurious to plants; to ascertain this, the ammonium compound was compared with guano as to its action on crops, and several plants were manured with guano to which ammonium thiocyanate was added, but no evil consequences were observed so long as the quantity was not more than 10 kilos. per hectare for rape, peas, and turnips, nor more than 20 kilos. for winter rye. In another set of experiments, crude ammonium superphosphate was tried against superphosphate to which ammonium sulphate had been added, and with a similar result, that no harm was done so long as the thiocyanate did not exceed a definite amount, but rather otherwise; and that of the plants employed, potatoes and maize were the most susceptible to the harmful action of the thiocyanate. E. W. P.

**Sulphuric Acid as a Manure.** By H. FRESSENIUS and STOCKS (*Bied. Centr.*, 1884, 160—162).—Fresenius considers that sulphuric acid is only valuable as a manure in soils which are free from lime, but rich in phosphates (*Abstr.*, 1883, 681). Stocks experimented with rye on sandy soil, meslin and barley on good loam, giving to the first two crops 96 kilos. acid, and 48 kilos. Chili saltpetre per hectare, whilst the third crop received 96 and 360 kilos., the results being that although there was an increase, yet that increase did not compensate for the expense.

Another writer composted dead “Damm” soil with acid, and gave it to barley with clover and to sugar-beet; a good yield was obtained, but this is ascribed to the favourable weather and not to the manure. He proposes to allow the compost to ripen by aid of the atmosphere, and not by acid. E. W. P.

**Krugite as Manure for Potatoes.** By J. KARBE (*Bied. Centr.*, 1884, 210).—Four centners of krugite applied in addition to a light dressing of farmyard manure and  $1\frac{3}{4}$  centners bone-meal per morgen, brought an increase of tubers but of lower starch-contents; the absolute yield of starch, however, was increased by 2 centners per morgen. E. W. P.

**Sodium Chloride as a Manure.** (*Bied. Centr.*, 1884, 209).—Stronger applications than 2 kilos. per fruit tree in moist weather is not advisable, and none should be given in dry weather. E. W. P.

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## Analytical Chemistry.

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**Ammonium Fluoride as a Blowpipe Reagent.** By N. W. LORD (*Chem. News*, **49**, 253).—A few grains of ammonium fluoride are added to a drop of sulphuric acid on a piece of platinum, the powdered mineral to be tested is then mixed in to form a paste. This is heated gently near the lower part of the flame in a platinum loop. By this means, and with the aid of a hand spectroscope, boron, potassium, sodium, and lithium are readily detected, if present, even in traces.  
D. A. L.

**Flashing Test for Gunpowder.** By C. E. MUNROE (*Chem. News*, **49**, 251—252).—Several methods of testing the quality of gunpowder are described, but in the author's words, the flashing test is the simplest, readiest, and, in the hands of an expert, the best test for the incorporation of powder; therefore, it was deemed desirable to have permanent records of such tests. With this object in view, the following method is recommended:—Pieces of paper coloured with Turnbull's blue (similar to the paper used in the "Blue Print Process" of photography) about 20 cm. square, are moistened, and placed on a sheet of glass or copper; the powder is filled evenly into a truncated leaden cone, 3 cm. capacity; this is inverted on the paper and removed, when the powder is left in a conical heap, and is fired by means of a hot iron, copper, or platinum wire, and after 30 seconds the paper is washed under a jet of water. Good powders produce a blackening and bleaching, where the heap comes in contact with the paper, whilst fine spots (and a few smudches) are uniformly distributed over the whole surface of the paper, which then has the appearance of being a paler blue, with occasional spots and streaks; badly incorporated powders give rise to spots of irregular shape and distribution. This results from the combustion being more regular the finer the ingredients and the more uniform and intimate the mixture is. The action is due to the formation of alkaline carbonates during the combustion of gunpowder. The paper is prepared by sponging it evenly out of contact with sun (day) light, with a mixture of a solution of potassium ferricyanide and ammonium ferrous citrate; it is then allowed to dry spontaneously, and the blue colour is developed by four or five hours' exposure to strong sunlight. For use, the paper is immersed in a stream of water for five minutes, put on the glass plate, and excess of moisture removed by filter or blotting paper.  
D. A. L.

**Estimation of Moisture in Amylaceous Matters.** By L. BONDONNEAU (*Compt. rend.*, **98**, 153—155).—To avoid errors in the estimation of moisture in starches, &c., the substance should, if neutral, be very slowly raised (1 hour required) to the temperature of 100°; but if it be distinctly acid, then that acid should previously be neutralised by mixing the substance with a little distilled water, to which a drop or two of ammonia has been added, and the drying is

then effected at a temperature not exceeding  $40^{\circ}$ , until it is nearly complete, when the heat is slowly increased to  $100^{\circ}$ .

R. R.

**Examination of Potash.** By H. HAGER (*Dingl. polyt. J.*, **252**, 86).—On adding silver nitrate to a 5 per cent. solution of potassium carbonate, a yellowish-white precipitate is formed, which is white when potassium hydrogen carbonate is present. On placing the test-tube in hot water, the precipitate should remain unaltered; when however sulphides, traces of sulphites, or thiosulphates are present, it assumes a grey, brown, or black colour.

D. B.

**Examination of Gas Liquor.** By S. DYSON (*Dingl. polyt. J.*, **251**, 457—459).—According to the author, the following substances may be expected to occur in gas liquor:—Ammonium sulphide, ammonium carbonate, ammonium chloride, ammonium thiocyanate, ammonium thiosulphate, ammonium sulphite, ammonium thiocarbonate, ammonium sulphate, ammonium ferrocyanide, ammonium cyanide, and ammonium acetate.

To detect ammonium thiocarbonate, zinc sulphate is added, and the precipitate filtered off and washed with cold water into a small flask connected with a condenser. On heating it, the zinc thiocarbonate is split up, carbon bisulphide being evolved, which is readily recognised by its odour, and if necessary its quantity may be determined with triethylphosphine, and weighed as  $\text{PET}_3\text{CS}_2$ . For the determination of ammonium thiocyanate, gas liquor is treated with zinc sulphate, the solution filtered, and the filtrate tested with ferric chloride. For the detection of ammonium thiosulphate, gas liquor is treated with zinc sulphate, the solution filtered, and barium chloride added to the filtrate. The filtrate is acidulated with hydrochloric acid and heated. Sulphur separates with evolution of sulphurous anhydride. By precipitating the sulphides with zinc sulphate, acidulating the filtrate with acetic acid, and adding sodium nitroprusside, potassium ferrocyanide gives a purple-red precipitate if sulphites are present. For the detection of chlorine in gas liquor, zinc sulphate is added, the solution filtered, and ferrous and copper sulphate added to the filtrate. The solution is again filtered, acidulated with nitric acid, and tested for chlorine with silver nitrate. To detect ammonium acetate, the liquor is evaporated to dryness, the residue taken up with water, treated with a hot saturated solution of silver sulphate, filtered, washed with hot water, and the filtrate distilled with dilute sulphuric acid. The distillate contains the acetic acid.

A sample of gas liquor from Leeds registered 4.15° Twaddell = 1.0207 sp. gr. at  $22^{\circ}$ . It contained sulphides, carbonates, chlorides, thiocyanates, thiosulphates, sulphates, and ferrocyanides. For the quantitative determination of the ammonia, 25 c.c. of the gas liquor were distilled with magnesia (Lunge, this vol., 776). For the determination of carbonic anhydride, 50 c.c. of the liquor are precipitated with calcium chloride. The precipitated calcium carbonate is filtered off, dissolved in 50 c.c. standard hydrochloric acid, and the solution titrated back with soda. To determine the chlorine quantitatively, 50 c.c. are evaporated to dryness, the residue is taken up

with water and filtered; the filtrate is then mixed with a solution of ferrous sulphate and copper sulphate, filtered, treated with nitric acid and silver nitrate, and the precipitate boiled, collected, and weighed. For the determination of the total sulphur, 25 c.c. of the liquor are treated gradually with water, acidulated with hydrochloric acid, and containing an excess of bromine; the excess of bromine is expelled by boiling, and the solution filtered and precipitated with barium chloride. The sulphides are determined by adding zinc sulphate and ammonium chloride to 25 c.c. of the liquor, filtering, washing the precipitate with water slightly acidulated with hydrochloric acid and containing an excess of bromine, heating to expel the excess of bromine, filtering, and adding barium chloride to the filtrate. For the determination of the thiocyanates, 50 c.c. are evaporated to dryness, the residue heated at  $100^{\circ}$  for four hours, then extracted with alcohol, the latter expelled by evaporation, the residue taken up with water, filtered, and precipitated with sulphurous acid and copper sulphate:  $2\text{NH}_4\text{CNS} + 2\text{CuSO}_4 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} = \text{Cu}_2(\text{CNS})_2 + (\text{NH}_4)_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$ . The precipitated cuprous thiocyanate is dissolved in nitric acid and thrown down with sodium hydroxide; the resulting cupric oxide, when multiplied by 0.96, gives the equivalent amount of ammonium thiocyanate. The sulphates are determined by evaporating 250 c.c. of gas liquor to dryness, adding water, removing the sulphides with zinc oxide, and precipitating the sulphates in the filtrate with barium chloride. To determine the ferrocyanides, 250 c.c. are evaporated, the residue dissolved in water, the solution filtered, and ferric chloride added to the filtrate. The precipitate is decomposed with caustic soda, and the resulting ferric oxide titrated with potassium permanganate. 1 litre of gas liquor treated in this way was found to contain—

Total ammonia .....	20.45	grams	
Total sulphur.....	3.92	"	
Ammonium sulphide ....	3.03	"	
,, carbonate ....	39.16	"	
,, chloride.....	14.23	"	
,, thiocyanate ..	1.80	"	
,, sulphate ....	0.19	"	
,, thiosulphate ..	2.80	"	
,, ferrocyanide ..	0.41	"	D. B.

**Estimation of Phosphoric Acid: Oxalic Acid Method as Compared with the Molybdic Method.** By D. LINDO (*Chem. News*, 49, 247—249).—From the results of previous experiments (this vol., 493—497) it is assumed that the molybdic method properly conducted can be safely taken as a standard. Therefore in the present communication several results are published of analyses of phosphatic mineral manures by the oxalic and molybdic methods. From these, it is inferred that as a rule the oxalic acid method does not give strictly accurate results, owing to the practical impossibility of removing all the silica from solution; and a minute quantity of this substance in the presence of alumina is sufficient to impair the result.

Ferric oxide does not act in this way, except when present in notable quantities. Aluminium silicate is slightly soluble in ammonium citrate, but is precipitated by magnesia mixture. Silica should also be removed, as completely as possible, before adding ammonium molybdate. In order to avoid any inconvenience with regard to lime, with the oxalic acid method, the author proceeds as follows: Nearly neutralise with ammonia, precipitate with oxalate, heat, filter, concentrate, filter again, make up filtrate to usual volume, add 1.5 to 2 grams citric acid, then ammonia and magnesia mixture. Ammonium citrate retards the precipitation of calcium oxalate considerably; therefore if the phosphoric precipitate is filtered off after four hours, or when sufficient excess of magnesium mixture is employed, two hours is long enough: there is no fear of any calcium being precipitated. The methods employed are fully described. D. A. L.

**Estimation of the Fuel Value of Coal according to Scheurer-Kestner.** By F. STOHMANN (*Dingl. polyt. J.*, 252, 73—78).—This is a reply to Scheurer-Kestner's criticisms that have appeared on the results of some observations made by the author with a new apparatus which Scheurer-Kestner considers to be only a modification of Frankland's calorimeter discarded by the inventor as inaccurate.

D. B.

**Estimation of Starch and Glucose in Food.** By C. FAULENBACH (*Bied. Centr.*, 1884, 71).—This is a modification of the method of Medicus. In order to obtain the starch in a soluble form, a solution of diastase is prepared in the following manner:— $3\frac{1}{2}$  kilos. of new malt is pounded, mixed with 2 litres of water and 4 litres of glycerol, digested for eight days, decanted, pressed, and filtered. 5 drops of this solution is sufficient to transform 1 gram of starch: 15 drops contain 1 mm. of sugar, and the author deducts that proportion from the result. After the transformation of the starch, the liquid is diluted to a determined volume, filtered, and a portion inverted with hydrochloric acid; after exact neutralisation, the quantity taken is diluted so that it may contain 0.1 to 0.2 per cent. sugar; the reduction proportion between Fehling's solution and glucose stands at 100 to 0.509. Titration is first tried with 10 c.c. of sugar solution and varying quantities of Fehling's solution; 40 c.c. are used for the final estimation.

J. F.

**Examination of Cane-sugar and Dextrose; Decolorising Dextrose Solutions.** By CASAMAJOR and others (*Bied. Centr.*, 1884, 198).—Place the doubtful cane-sugar in a cup, add sufficient water to make it moist, heat to 50—100°. In 10 minutes the adulterated (with dextrose) sugar will form a gummy mass, which when cooled will still remain gummy, whilst the pure cane-sugar becomes drier than when hot. A more exact test is that of polarisation, when dextrose shows rotatory power immediately after solution, which is not the case with cane-sugar. Fehling's solution shows in common solutions the presence of a reducing agent to the extent of 5 per cent., whilst in adulterated sugar 20 per cent. is found. To decolorise grape-sugar solutions, v. Korwin and Rosenblum add potassium permanganate equal

to 0·2 per cent. of the weight of starch; this is added to sugar solution at 45°, to which chalk has been added, and then the precipitate is filtered off, and the liquid evaporated down to sp. gr. 1·5 at 45°.

E. W. P.

**Testing of Yeast.** By E. MEISSEL (*Bied. Centr.*, 1884, 205—207).—A mixture of 400 grams pure cane-sugar, 25 grams ammonium hydrogen phosphate, and 25 grams potassium hydrogen phosphate is prepared, and of this 4·5 grams, dissolved in 50 c.c. plain water, is introduced into a light 70—80 cm. flask fitted with a cork, through which two tubes pass. One of these is bent at right angles, the longer portion reaching nearly to the bottom of the flask, whilst the shorter part may be closed by a stopper; the other tube carries a calcium chloride tube. 1 gram of the yeast is then placed in the flask, and the whole well shaken. After weighing and heating at 30° for six hours, the flask and its contents are rapidly cooled, the stopper opened, the carbonic anhydride removed, and the whole again weighed. The results thus obtained (which represent the fermentative power of the yeast) are compared with those obtained by the use of an ideal and normal yeast producing from 4·5 grams of the sugar mixture, 1·75 grams CO<sub>2</sub>, thus:  $\text{CO}_2 \text{ found} \times \frac{100}{1\cdot75} = \text{fermentative power.}$

E. W. P.

**Examination of Olive Oil.** By S. CARPI (*Dingl. polyt. J.*, 252, 87).—The author has found that on cooling cotton-seed oil for three hours at -20° it is less firm in consistence than olive-oil treated in the same manner.

D. B.

**Examination of Tannin Extracts.** By F. SIMAND (*Dingl. polyt. J.*, 252, 471).—For the estimation of tannin in tannin extracts the use of Löwenthal's improved method (*Abstr.*, 1883, 391), is

Extract of	Dissolved in cold H <sub>2</sub> O. Tannin.	Dissolved in hot H <sub>2</sub> O. Tannin.	Difference on 100 pts. of extract.	Calculated on 100 pts. tannin.	Remarks.
	Per cent.	Per cent.			
Quebracho wood (solid) .....	70·09	73·08	2·99	4·09	The commercial product dried before analysis. Prepared by the author and dried before analysis. 18° B., prepared by the author.
Valonia (solid)	68·59	70·44	1·85	2·62	
Oak wood .....	15·09	15·47	0·38	2·45	
Fir wood.....	13·72	14·31	0·59	4·13	
Oak bark.....	23·72	24·37	0·65	2·67	
Chestnut wood.	22·68	23·52	0·84	3·57	Commercial ex- tract.
Sumach.....	10·75	13·38	2·63	19·66	

strongly recommended. It is shown, however, that when the solution is prepared with hot water, a larger percentage of tannin is obtained than when the extract is dissolved in cold water. Hence in investigating tannin extracts, it should always be stated whether hot or cold water has been used for dissolving the extract. The subjoined table (p. 931) gives the author's results.

D. B.

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## Technical Chemistry.

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**Self-purification of Sewage-contaminated Rivers.** By F. HULWA (*Bied. Centr.*, 1884, 1—2).—This paper is the result of investigations made by the author on the water of the River Oder before it entered and after it had passed through the city of Breslau, receiving in its transit the sewage of the city. The standard of purity adopted was a minimum (in 100,000 parts) of 50 parts total residue, 1·5 nitric acid, 3 chlorine and traces of ammonia and albuminoid ammonia, 0·25 of oxygen to oxidise organic matter, and 18° to 20° of hardness (German scale).

According to this scale, the water of the river before entering Breslau, although slightly contaminated, yielded an excellent drinking water after being filtered. In its progress through the city the river shows increasing pollution, and at its exit was greatly polluted; a short distance down the river the effects of dilution became evident; the self-purification of the river by the combined action of the oxygen of the air and of vegetable and animal life in the stream itself were very marked, the impurities diminishing so rapidly that at 14 kilos. distant from the city the water was as pure as when it entered it, neither chemical nor microscopical tests showing serious impurity. The author thinks it a mistake to forbid the outflow of sewage into rivers, provided that the outfall is below the city, and the rapidity and volume of the stream are sufficient to carry the sewage to such a distance as will allow the operation of natural causes of purification.

J. F.

**Preservative Effect of Ether- and Chloroform-vapour on Organic Substances.** By R. DUBOIS (*Bied. Centr.*, 1884, 72).—Pears were placed under bell-glasses, the air of which was saturated with the vapour of chloroform, ether, alcohol, or water. The fruit in the first two vapours became discoloured in a few hours; in alcohol-vapour after two or three days, in the water-vapour they preserved their appearance many days. Weighed after many months the loss was: Chloroform, 6·75 per cent.; ether, 2·5 per cent.; alcohol, 0·6 per cent.; and water-vapour, 1·14 per cent. The fruit in the latter case was covered with a coat of mould.

In other experiments with anatomical preparations and whole animals, under glasses filled with ether-vapour, there was no decom-

position, only a loss of moisture. Blood so treated showed no alteration of the corpuscles after a long time—they were only drawn together somewhat more closely. J. F.

**Influence of Calcination and of Carbonic Anhydride on the Setting of Hydraulic Cements.** By E. LANDRIN (*Compt. rend.*, 98, 1053—1055. Compare Abstr., 1883, 754, 830).—The silicate,  $\text{SiO}_2, 2\text{CaO}$ , was prepared by heating pure lime and silica in the proper proportions at a bright-red heat for several hours. The product remained pulverulent, but was completely soluble in hydrochloric acid. In one case only was it scoriaceous as described by Berthier. When this silicate is moistened with water, no heat is developed, and after 24 hours it acquires the consistency of soap, but its hardness is not increased even after many months. If, however, the substance, either freshly prepared or after it has been in contact with water for some time, is brought in contact with water charged with carbonic acid, it rapidly sets and the hardness of the mass increases as the absorption of carbonic anhydride progresses.

The silicate,  $\text{SiO}_2, \text{CaO}$ , was obtained in three forms by roasting its constituents at a high temperature for different lengths of time, viz., A, pulverulent; B, fritted; and C, fused. All these products were readily and completely soluble in hydrochloric acid. When finely powdered and moistened with water, A and B set without development of heat in exactly the same manner as mixtures of hydraulic silica and lime, but C did not set even after immersion in water for several years. If, however, they are placed in water charged with carbonic acid, all three varieties set and become extremely hard.

It is evident that calcium silicates set with difficulty after being heated to a high temperature, and in all cases do not harden under water. In order to obtain the maximum hydraulicity, the process of calcination should be continued sufficiently long to convert all the silica into hydraulic silica without fusing the product. The absorption of carbonic anhydride is an essential factor in the setting of hydraulic cements, and is the only factor which determines the ultimate hardening of the mass. C. H. B.

**Application of Electricity in Chemical Industry.** By F. FISCHER (*Dingl. polyt. J.*, 251, 418—424).—Hermann (Ger. Pat. 24,682, April, 1883) recommends the electrolytical deposition of zinc from dilute solutions of the sulphate by the aid of potassium, sodium, ammonium, strontium, magnesium, or aluminium sulphates, used singly or mixed together. Kiliani states that during the electrolysis of a solution of zinc sulphate of 1.38 sp. gr. (the anodes and cathodes consisted of zinc plates), the evolution of gas is greatest with a weak current, diminishing with an increasing current, and ceasing when 3 mgrms. of zinc are deposited on 1 square centimetre pole surface per minute. The deposits obtained with strong currents were firm. From a 10 per cent. solution, the precipitate was obtained in the best form with a current of from 0.4 to 0.2 mgrm. zinc. From weak solutions, the zinc was always deposited in a spongy condition with evolution of much hydrogen. Kiliani concludes that the size of the pole

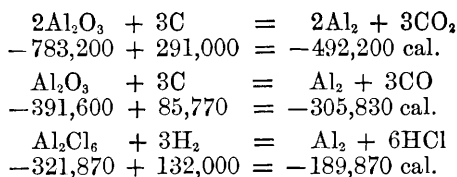
surfaces depends on the intensity of the current and the concentration of the solution.

For the extraction of metals from ores, Blas and Miest employed a process which depends on the fact that the natural sulphides conduct electricity when they are rolled into plates whilst hot. These plates are then suspended as anodes in a suitable bath. For the separation of zinc from blende the bath consists of zinc sulphate, and the following reaction takes place:— $\text{ZnSO}_4 + \text{ZnS} = \text{Zn} + \text{S} + \text{ZnSO}_4$ . The advantages of this process are (1) the ores do not require to be roasted; (2) the sulphur is obtained as such; (3) less current energy is required for the decomposition of zinc sulphide. In the case of galena, a bath of lead nitrate is used. Marchese has patented a similar process, the essential difference being the suspension in the depositing tanks of the ores in lumps or small pieces filled into iron baskets.

Referring to the electrolytic extraction of copper, the author states that the firm of Siemens and Halske of Berlin have five machines  $C_1$ , each with 12 baths in action at the Oker Works. Each machine is worked with a water power of 4 to 5 e. and deposits 1 kilo. copper per cell per hour, *i.e.*, about 300 kilos. per diem. At the North German Refining Works in Hamburg, six Gramme machines (No. 1) and one Wohlwill machine are in operation precipitating 2500 kilos. of copper daily. Oescher and Mesdach have constructed a Gramme machine according to Wohlwill's instructions, which yields 800 kilos. of copper daily. Hilarion Roux in Marseilles works with a No. 1 Gramme machine (5 e.) connected with 40 baths having 900 square meters anode surface; the cathodes are only 0.5 mm. thick, and are 5 cm. from the anodes. The machine makes 850 revolutions a minute, consumes 240 kilos. coal per day, and deposits with 8 volts and 300 ampères 250 kilos. of refined copper.

Keith's process for refining lead is worked by the Electro-metal Refining Company in New York. The bath consists of lead sulphate dissolved in sodium acetate; gold, silver, and antimony are retained by the anode.

The deposition of aluminium by electrolytic means is discussed by the author. According to Weldon, the cost of preparing alumina from bauxite at Pechiney's works at Salindres, amounts to 9.7 per cent., that of the preparation of double chloride of aluminium and sodium 33.4 per cent., and for the decomposition of the double chloride with metallic sodium 56.9 per cent. of the total expenditure. The manufacture of 1 kilo. sodium costs about 7 shillings, the largest item being for the costs of the vessels in which the sodium carbonate is heated with powdered charcoal, and which are so rapidly destroyed that their cost stands for one-half the total cost of sodium, and a third of the total cost of aluminium. It is further considered an impossibility to reduce alumina by carbon, for the reactions which occur correspond with the following numbers:—



That in spite of these unfavourable thermochemical relations, sodium can be formed from sodium carbonate and carbon is explained by Weldon as follows:—When a mixture of sodium carbonate and carbon is heated intensely, some of the sodium oxide becomes dissociated, and the carbon then combines with the oxygen, sodium being liberated. The temperature required for the dissociation of  $\text{Al}_2\text{O}_3$  is, however, considered to be unattainable on a large scale.

The author is of opinion that if this explanation is correct there should be no difficulty in obtaining this dissociation temperature by the aid of the electric furnace. Moreover the reaction  $\text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2$  corresponds with  $-136,800 + 97,000 = -39,890$  cal., and yet it takes place when steam is passed over lignite coke heated to  $300\text{--}350^\circ$ , a temperature at which steam could not undergo dissociation; the reaction  $\text{ZnO} + \text{C} = \text{Zn} + \text{CO}$  yields  $-85,430 + 28,590 = -56,840$  cal. If therefore heat be supplied by external means reactions accompanied by the absorption of heat would be possible.

For the separation of iron from the solutions of aluminium sulphate, sodium sulphate, &c., Löwig and Co. in Goldschmieden deposit the iron electrolytically. When treating solutions of sulphates, the anode is to be of lead. The separation of the iron does not take place unless the production of oxygen at the anode can be almost entirely prevented. This is effected either by using an anode with a large surface or by causing as much resistance as possible to be offered to the passage of the current at the anode.

D. B.

**The so-called Burning of Iron and Steel.** By A. LEDEBUHR (*Dingl. polyt. J.*, 251, 506—509).—The author attributes the burning of iron to prolonged exposure to the action of red-hot fuel gases. A cast-iron plate which had been exposed for several years to the flame of a coal fire had the following composition:—

Graphite .....	0.960
Combined carbon .....	—
Iron .....	68.386
Sulphur .....	0.079
Arsenic .....	0.056
Phosphorus .....	0.269
Copper, nickel .....	0.125
Oxygen combined with iron, sulphur, arsenic, phosphorus, copper, and nickel .....	27.804
Manganous oxide .....	0.030
Silicic acid .....	2.328

When wrought iron is heated to or near its fusing point and cooled slowly, without being welded, it becomes burnt iron. A piece of

melted wrought iron taken from the bottom of a gas-mill furnace at Riesa gave on analysis—

C.	Si.	P.	S.	O.	Mn.	Cu.	CoNi.
0.052	—	0.223	—	0.177	—	0.450	0.157

From a series of experiments on the burning of iron and steel, the author infers that the carbon in steel containing small quantities of manganese and silicon, burns away and thus reduces the hardness, firmness, and elasticity of the steel, whilst the carbon in steel rich in silicon and manganese does not burn away but is probably oxidised, which operation alters the properties of steel. Iron, however, is not oxidised in a similar manner. D. B.

**Process for Phosphorising Bronze or Brass.** By J. WHITING (*Dingl. polyt. J.*, 251, 431).—Bronze or brass wire is placed for some time in a solution of 0.125 to 5 per cent. phosphorus dissolved in ether, carbon bisulphide, or olive-oil, 5 to 10 per cent. of sulphuric acid, and 85 to 95 per cent. water. The metal takes up phosphorus. The wire is then drawn a size finer and introduced into a closed retort, the bottom is covered with a thin layer of phosphorus so that the resulting vapours come in contact with the wire. After this the wire is packed in wood-charcoal and ignited, and heated until it softens, and can be drawn a size still smaller. This treatment is alternately repeated until the wire has been reduced to the desired fineness. Wire prepared in this manner is said to be more indestructible, takes a higher polish, and is less subject to corrosion. D. B.

**Researches on Russian Petroleum and Petroleum Lamps.** By J. BIEL (*Dingl. polyt. J.*, 252, 119—123).—It is shown that the smaller the amount of luminosity afforded by a petroleum lamp the greater is the consumption of oil calculated on 100 units of illuminating power produced. A lamp burns proportionately the smallest quantity of petroleum when it develops its full degree of brilliancy. The length of wick up which the petroleum has to travel, that is, the capillary attraction of petroleum, depends on the boiling point or the percentage of oils boiling above 270°, and is influenced by the diameter of the wick. In order to adapt the German round burners to Russian petroleum it is necessary to shorten the lower part of the glass chimney. Flat burners consume from 34 to 38 per cent. more oil than round burners, the luminosity being the same in each case. Efforts should be made to induce the Russian petroleum industry to produce a petroleum oil for general use which shall not give off an inflammable vapour under 35°, and contain at the same time up to 30 per cent. of heavy oils. It is further recommended to determine the quality of petroleum by distillation according to a uniform standard. D. B.

**Fractional Distillation of Mineral Oils in a Current of Steam.** By F. RASINSKI (*J. pr. Chem.* [2], 29, 39—41).—The steam is introduced by means of a tube passing to the bottom of the dis-

tillation flask. The mixture of water and hydrocarbon vapours is passed through long cooling tubes and then washed in Mendelejeff's flasks. When the flasks become full, the steam is shut off and their contents are returned to the distillation flask. The mixture of vapours issuing from the last of the series of flasks is, after cooling, collected in portions of 65—70 c.c., and the sp. gr. determined. Also the proportion between the weights of water and oil is ascertained. The numbers obtained are used for coordinates in describing the curve by which each distillation is represented. The relative volume for the same sp. gr. becomes less each successive distillation, until a certain point is reached when for some time it exhibits no marked alteration. The deflection of the curves corresponds very closely with that observed in the ordinary process of distillation. The relative volume at first increases rapidly for the same sp. gr., then falls slowly, as is exemplified by the following table:—

	0·7700	0·7800	0·7900	0·8000	0·8100	0·8200	0·8300	0·8400	0·8500	0·8550
1 .....	—	—	—	135	215	330	570	1100	2500	—
2 .....	—	37	56	90	140	212	420	960	1850	3300
3 .....	30	36	54	84	127	208	343	825	1625	—
4 .....	27	35	52	78	118	184	335	—	—	—
5 .....	24	34	56	70	114	172	321	—	—	—
6 .....	22	34	48	69	105	169	—	—	—	—
7 .....	22	33	47	69	105	169	—	—	—	—

J. I. W.

**Caoutchouc and its Applications.** (*Dingl. polyt. J.*, 251, 459—461.)—For the manufacture of sets of elastic teeth, Bentelrock uses soft vulcanised caoutchouc for the gum, whilst the teeth and chewing surfaces are made of hard caoutchouc. According to De Tour-du Brueil the vulcanising of articles prepared from caoutchouc and sulphur can be performed in a boiling solution of calcium chloride.

Kent works up india-rubber waste by grinding and mixing it with water, and thereby separates the india-rubber from the specifically heavier impurities.

According to Burghardt caoutchouc is gradually oxidised in the air, forming a hard resin soluble in alkalis and containing 27·3 per cent. oxygen and a resinous mass containing 20 per cent. oxygen and insoluble in alkalis and benzene. Perfectly new and fresh vulcanised caoutchouc contains about 3 per cent. of the first resin, but is free from the insoluble resin described above. Good caoutchouc should not contain more than 0·5 per cent. water; brittle and hard caoutchouc contains from 5 to 10 per cent., which is given off on heating at 100° to 120°. The carbon in decomposed caoutchouc is reduced and the quantity of oxygen increased as may be seen from the following analyses. No. I is a normal sample; Nos. II to IV were more or less damaged and brittle, No. V was very hard and brittle:—

	I.	II.	III.	IV.	V.
Carbon ....	77.91	72.53	70.43	65.09	64.00
Hydrogen ..	10.33	11.31	10.59	10.04	9.26
Sulphur ....	5.15	1.97	3.14	1.95	2.28
Oxygen ....	6.61	14.19	15.84	22.96	24.46

The destruction of caoutchouc is facilitated by painting it with oil, especially olive-oil or palm-oil, as they promote oxidation. Certain dyes are also injurious to caoutchouc, particularly if they contain copper compounds. If caoutchouc is vulcanised with more than from 2 to 2.5 per cent. of sulphur, the excess is oxidised by the oxygen of the air into sulphuric acid which then attacks the caoutchouc. The process of boiling the caoutchouc in caustic alkalis with a view to eliminate the excess of sulphur is injurious on account of its rendering the surface porous, so that the oxygen of the air can more easily act thereon. A better method has been worked out by Rowley who mixes only the theoretical amount of sulphur (2 to 2.5 per cent.) with caoutchouc, and vulcanises either in an aqueous solution of ammonia (12 per cent.  $\text{NH}_3$ ) or in the gas itself in the presence of steam.

Gernez has patented methods of making and treating various mixtures of either india-rubber or gutta-percha with sulphur, camphor, gum kauri, and the farina of mustard deprived of its oils and husks.

D. B.

**Purification of Glycerol.** By C. MOLDENHAUER and C. HEINZERLING (*Dingl. polyt. J.*, 252, 86).—The authors evaporate crude glycerol or soap-leys to dryness at a low temperature, treat the residue with 1–2 parts absolute alcohol, add 1–10 per cent. anhydrous sodium carbonate, and separate the deposited salts by filtration. The resulting alcoholic solution is then acidulated with sulphuric acid, the sodium salt separated, and the solution treated with lead oxide or lead salts, in order to remove the chlorine. The alcohol is then expelled from the solution by distillation in suitable stills.

D. B.

**Improvement of Inferior Wine by Addition of the Husks of Superior Grapes.** By J. NESSLER (*Bied. Centr.*, 1884, 59–60).—The wine of 1882 was deficient in alcohol and contained much acid. The endeavour to improve it by the addition of the mark or pressed residue of the 1883 grapes was very successful. The percentage of alcohol was raised, the acid diminished, and many impurities removed. Certain precautions as to removal of stalks, &c., are recommended.

J. F.

**Reduction of Extractive Matter by Clearing of Wine.** By K. PORTELE (*Bied. Centr.*, 1884, 57–59).—The author found that when red wine is cleared with gelatin the percentage of extract is considerably reduced, and so really good natural wines may be reduced below the minimum, 65 per cent. of solid extract.

The clearing of wine by gelatin has a considerable effect on the colour of inferior qualities, some of these being quite decolorised.

The treatment of red wine by Pasteur's method also affects the colour, but the author's opinion is different from that of other authorities, and the question remains undecided. J. F.

**Fermentative Strength of Beer Yeast in Distillery Mash.** By K. KRUIS (*Bied. Centr.*, 1884, 72).—The experiments were made in order to find if beer barm could be used to replace the artificial ferments used by distillers, and it was found that it produced a tolerably energetic fermentation, and in a moderately short time accommodates itself to the temperature and conditions of distillers' mash. J. F.

**Action of Air on Beer Yeast.** By D. COCHIN (*Bied. Centr.*, 1884, 203—205).—The cellular membrane of the yeast permits the passage of sugar solution, and after a short time fermentation commences; if this endosmose occurs at the ordinary pressure, the solution within is of the same strength as that without, but if the air be removed, then the internal solution is richer in sugar than the external. When there is no free admission of air to yeast, its action on sugar is considerably reduced. E. W. P.

**Beet Sugar.** By E. v. LIPPMANN and others (*Bied. Centr.*, 1884, 201—203).—From the incrustation of lime salts in the evaporating pans, Lippmann has obtained, amongst other acids, a new acid which he believes to be closely allied to, if not identical with, hydroxycitronic acid.

A. Nord states that to prepare strontianite in a proper condition for purifying sugar, it must be powdered, mixed with sawdust and "a small quantity of a cheap vegetable glutinous material," and worked into bricks, which when dried are burnt. Steffens recovers the ammonia contained in the alcohol employed for the removal of molasses, by adding sulphuric acid, when the sulphate formed is precipitated after the alcohol has been sufficiently concentrated.

E. W. P.

**Employment of Magnesium Sulphite and Ferric Chloride in Sugar Factories.** By R. BERGREEN and O. LICHT (*Bied. Centr.*, 1884, 201).—Basic magnesium sulphite,  $\text{MgSO}_3 + 2\text{Mg}(\text{OH})_2$ , is employed in preference to the free acid, and it is prepared by passing sulphur dioxide into water, holding magnesia in suspension. Licht prefers to use ferric chloride instead of barium chloride for purifying crude syrups, because the organic acids are more easily precipitated, and the separation by means of lime facilitated.

E. W. P.

**Recovery of Sugar from Molasses by Means of Lime.** (*Dingl. polyt. J.*, 251, 373—380 and 415—418).—In order to diminish the quantity of insoluble lime salts produced in the preparation of calcium saccharate, and also during the washing, Manoury boils the molasses with lime and decomposes the resulting lime salts with sodium carbonate, calcium carbonate and alkaline salts being formed. The latter, however, are soluble, so that a certain amount of organic non-saccharine matter is removed from the saccharate; had this been



in combination with lime it would have been insoluble in dilute alcohol, and have contaminated the sugar after saturation. The loss of sugar is mainly due to the fact that a portion of the sugar does not combine with sufficient lime to form tri-saccharate. It is shown that in the preparation of calcium saccharate, according to Eissfeldt's method, the smallest loss of sugar takes place. The purity of the saccharate depends largely on the mechanical procedure of the extraction. The impurity caused by the decomposition of the saccharate by potash salts of organic acids is unavoidable in all processes, and depends on the perfect combination of the sugar with the lime in the saccharate; but the further contamination of the saccharate by the action of the excess of caustic lime in the saccharate on the potash salts depends on the rapidity of the extraction. As the caustic lime is but sparingly soluble in dilute alcohol, it is possible to remove the potash salts, which are more readily soluble, before appreciable quantities of lime are dissolved. In the first portions of the liquors, the largest quantities of non-saccharine matter and sugar are dissolved in the following order:—

Non-saccharine.	Sugar.
Eissfeldt.	Manoury.
Manoury.	Weinrich.
Weinrich.	Scheibler-Seyferth.
Scheibler-Seyferth.	Eissfeldt.
Drevermann.	Drevermann.

For dissolving approximately equal quantities of non-saccharine matter at the commencement of the extraction, the parts of ley required are given, and the amount of sugar dissolved under it—

According to	I.	II.
	Parts.	Parts.
Manoury .....	1·00	2·89
Eissfeldt .....	1·18	1·00
Weinrich .....	1·81	2·79
Scheibler-Seyferth ..	7·01	3·97
Drevermann .....	8·18	3·20
Eissfeldt .....	1·00	—
Weinrich .....	2·79	—
Manoury .....	2·89	—
Drevermann .....	3·20	—
Scheibler-Seyferth ..	3·97	—

The first leys at the same time contain the largest quantities of free potash, so that here the largest quantities of lime salts are formed, but owing to the different solubilities of the potash salts and the calcium saccharate in dilute alcohol, the first leys also contain the largest amount of undecomposed alkali salts, which gradually disappear, owing to the fact that in the subsequent portions of the leys enough lime and calcium saccharate is dissolved to decompose the alkali salts still in solution. The production of free potash in the leys is mainly caused by the action of soluble monobasic saccharate on the alkali salts, although to some extent it depends also on the action of the dissolved calcium hydroxide on the alkali salts.

Whilst according to Lippmann in the substitution process for the production of tribasic saccharate by continued agitation of a solution of molasses and milk of lime, a soluble monobasic calcium saccharate is formed, which, on boiling, deposits part of the sugar in a tribasic form, it was found that on introducing finely-divided lime into a sugar solution an immediate formation of the same saccharate was effected. On examining this, Steffen has discovered a new reaction and based a new process thereon. In order to completely precipitate the sugar from a solution, it was found necessary to employ a solution of sugar saturated with lime, containing not less than 33 parts dissolved lime to 100 parts sugar. On introducing a fresh quantity of lime into this solution, the sugar contained therein is immediately precipitated in a granular form as tribasic calcium saccharate.

Wolters has patented a process for the recovery of sugar from aqueous solutions in the form of an insoluble tetrabasic calcium saccharate. For its production, it is necessary to avoid a rise of temperature during the mixing of the lime with the molasses. Over-burnt lime is ground and mixed with a quantity of an 8 or 10 per cent. solution of sugar, of which 1 mol. equals 3 mols. of lime. The mixture is then filtered, and the filtrate treated with 0.5 mol. lime. After careful agitation the mixture is decanted, when a precipitate is deposited composed of 1 of sugar and 4 of lime. D. B.

**Dubrunfaut's Lime Osmose Process.** By J. DE PUYDT (*Bied. Centr.*, 1884, 60—61).—This process has been tried in a factory and somewhat modified, with good results. The leading feature of the process is the addition of lime to the molasses or syrup, the sugar forms with it a sparingly soluble monocalcic saccharate, whilst the alkalies are expelled from their organic combinations, and are easily diffused. The modification now suggested is that instead of lime, calcium chloride should be used, which combines with potash and soda, the chlorides of which are so soluble. The syrup purified by osmose is then added to fresh juice, which is treated with lime and carbonic acid; sugar is obtained, and new syrup formed, the process being continuous. J. F.

**A Physical Property of Milk.** By G. RECKNAGEL (*Bied. Centr.*, 1884, 16—18).—The thickening of milk is irrespective of its temperature, and hitherto has not been much investigated; it cannot be assigned to the escape of gases, because old milk which has been boiled and cooled behaves in the same manner. In view of the importance of the sp. gr. of milk to public analysts and general control, the German Government directed the author to investigate the subject. He found that when milk was kept at a temperature of 15° the thickening process proceeded slowly and took two days to complete. The density of the milk was increased 0.8° to 1.5° of Quevenne's lactodensimeter, and varied with the richness of the milk; by cooling below 15° the process is hastened and is completed in six hours if the temperature is kept at 5° or below it.

When thickened milk is warmed, it breaks up into fragments; on cooling, it again thickens. As to the cause, the author does not think

it due to the formation of acid, as milk which has become acidified is of less sp. gr. than before; nor does he think it due to a breaking up of the milk globules, as a low temperature delays that operation and hastens the thickening: he thinks it is caused by the swelling of the casein, and finds an analogy in the behaviour of glue, which at low temperatures absorbs much water, which is expelled when the temperature is raised.

J. F.

**Blue Milk, Blue Cheese, and Ropy Milk.** By M. SCHMÖGER and others (*Bied. Centr.*, 1884, 196—198).—Cheese made from milk separated from centrifugal machines turns blue: this is not due to bacteria, but to iron removed from the drum; the same result can be obtained by adding ferric chloride to ordinary cheese: the blueing of milk is doubtless produced by the same cause. Schmitt prevents the blueing by disinfecting by means of sulphur dioxide. J. Reiset prevents the above mentioned appearance by adding to 10 litres milk 1 litre 1 per cent. acetic acid; this does not prevent the rise of cream nor damage the flavour of the butter. Another writer attributes the ropyness of milk to the use of bran as fodder.

E. W. P.

**Cheese from Skim-milk, with Foreign Fats added.** By C. HANSEN and others (*Bied. Centr.*, 1884, 199).—Skim-milk containing 0.15 per cent. fat is made into cheese with the addition of 1.5—2 per cent. oleomargarine. Schrodtt finds such artificial cheeses are not to be readily distinguished from pure cheese. Langfurth finds less volatile fatty acids in artificial American cheese than in pure sorts of English, Dutch, &c., origin.

E. W. P.

**Application of Electrolysis in Preparing Indigo Vats.** By F. GOPPELSROEDER (*Dingl. polyt. J.*, 251, 465—467).—In furtherance of his former researches on the use of electrolysis in dyeing and printing, the author gives a description of the method adopted by him for the preparation of the alkaline indigo vat. He mixes finely-divided indigo with a concentrated solution of caustic potash and fills a copper vessel half full with this mixture as also a porous cell, which is then placed into the copper vessel. The latter communicates with the negative pole of a galvanic battery or dynamo machine, whilst into the solution contained in the porous cell a large platinum plate is placed, which forms the positive pole. The apparatus is then warmed gently, and the current passed through for 3—4 hours. At the negative pole, *i.e.*, in the copper vessel, hydrogen is liberated with the formation of much froth and the characteristic odour of the indigo vat. The indigo-blue is converted into indigo-white, which dissolves in the alkaline solution. The resulting yellowish-green vat is then used for dyeing cotton fabrics indigo-blue.

D. B.

**Dyeing Cotton-yarn with Aniline-black in the Cold.** By A. RENARD (*Dingl. polyt. J.*, 251, 425—428).—The author describes a process for producing aniline-black on cotton without the application of heat. The ordinary method of dyeing cotton-yarns with aniline-black consists in introducing the material into a cold bath containing

aniline, hydrochloric acid, sulphuric acid, and potassium dichromate, and heating at 50—60° as soon as the colour begins to develop. In the author's process, the same substances are used, but the proportions are different. The best results are obtained with the following mixture:—For 100 kilos. cotton, 16 to 20 kilos. hydrochloric acid, 21° B; 20 kilos. sulphuric acid, 66° B.; 8 to 10 kilos. aniline oil; 14 to 20 kilos. potassium dichromate; and 10 kilos. ferrous sulphate. The presence of the latter is not absolutely necessary, but it helps to increase the stability of the colour. The amount of water used is much smaller than in the ordinary process, as the reaction must take place in a shorter time and without the help of heat: hence the form of the dye vats has to be altered, to admit of the smallest quantity of solution being employed. The aniline is mixed in the vat with hydrochloric acid previously diluted with an equal volume of water, the sulphuric acid diluted to the same degree is then added, and finally the solution of ferrous sulphate. The dichromate is dissolved in another portion of water. The yarns are boiled, washed, and wrung out, after which they are placed on reels fixed over the vat. The solution in the vat is diluted with water, and to it half the dichromate solution is added. The reels are then rotated for 1 to 1½ hours. The goods are now taken out of the vat; the remaining half of the chromium solution is added and the dyeing continued, until the desired shade is produced. The dyed fabric is then washed and boiled in a soap solution containing 5 grams of soap per litre, and about 2 per cent. sodium carbonate. The resulting black is sufficiently fast for all purposes, being unaltered in the air or when exposed to the action of dilute sulphurous acid. Bronze and blue blacks are produced in a similar manner: it is necessary, however, to use a smaller amount of chemicals and reduce the time of dyeing. The bronze colour is obtained by washing and drying the unsoaped cotton, whilst the blue-black is formed by treating the soaped fabric with sodium carbonate.

D. B.

**Preparation of Blue Colouring-matters.** (*Dingl. polyt. J.*, 252, 78—82.)—For the preparation of blue sulphuretted dye-stuffs, 10 kilos. dimethylaniline are dissolved in 10 litres hydrochloric acid of 21.5° B. and 50 litres water, and treated gradually with a solution of 7 kilos. sodium nitrite in 25 litres water. The product is mixed with an excess of ammonium sulphide (about 20 litres), heated, and agitated until the unattacked ammonium sulphide has been expelled. The mixture is then cooled, and the aqueous liquor separated from the resulting resinous sulphur compound by filtration (*Actien. Ges.f. Anil. Fab. Berlin*).

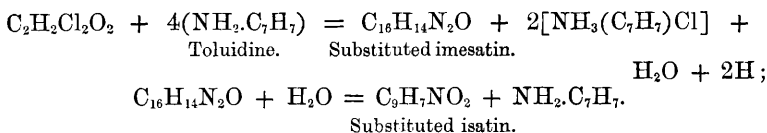
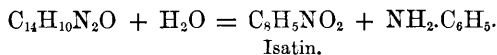
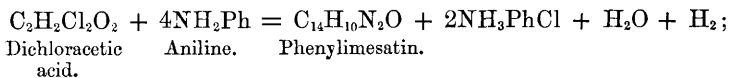
Bernthsen obtains a blue colouring-matter by heating 10 parts of diphenylamine with 4 parts of sulphur at 250—300°. Hydrogen sulphide is evolved and thiodiphenylamine obtained. The latter is purified by distillation and several crystallisations from alcohol. It is converted into a nitro-compound by treatment with 5 parts nitric acid of 40° B. On treating the nitro-derivative with acid stannous chloride (or other reducing agent), a colourless liquid is obtained containing the stannochloride of a leuco-base, and on oxidising this a violet colouring-matter is obtained. The dye-stuff may be fixed

directly on the animal fibre, and is adapted to the dyeing of animalised or tanned cotton fabrics.

For the preparation of orange dye-stuffs and their conversion into blue sulphuretted colouring-matters, Möhlau dissolves 14 kilos. nitrosodimethylaniline hydrochloride and 8.5 kilos. dimethylaniline in 45 kilos. warm hydrochloric acid of 1.16 sp. gr. On adding water to the mixture and neutralising the acid, the colouring matter is deposited. For the formation of the blue dye, the acid aqueous solution of rubifuscin is treated with a reducing agent (zinc, tin, iron, sulphurous anhydride, thiosulphates, ammonium sulphide, hydrogen sulphide) at the ordinary or an elevated temperature, until the conversion into a leuco-compound is completed.

Fischer treats trichlorobenzaldehyde (m. p. 100—110°) with dimethyl- or diethyl-aniline, and obtains crystallisable leuco-bases, which produce bluish-green colours on oxidation. On heating 1 part trichlorobenzaldehyde with from 2 to 3 parts dimethylaniline in the presence of zinc chloride, a new leuco-base is obtained, which has the composition  $C_{23}H_{23}Cl_3N_2$ , is sparingly soluble in water and alcohol, and crystallises from hot alcohol or benzene in needles melting at 128—129°. When this leuco-base is oxidised in an acid solution, it yields a colour base having the formula  $C_{23}H_{23}Cl_3N_2O$ . It forms crystalline salts, and imparts a bluish-green colour to the fibre.

Meyer describes the preparation of substituted isatins and their conversion into substituted indigo. He subjects aniline, toluidine, xyldine, cumidine, naphthylamine, their alkyl or halogen substitution products, or the corresponding diamines to the action of dichloro- (dibrom- or diiodo-) acetic acid or its amides. The direct products of the reaction are substituted imesatins, which readily give up the imido-group for oxygen when treated with strong acids or bases, yielding isatin or substituted isatin. The reactions are explained by the following equations:—



The resulting isatin or the substituted isatin may be converted into indigo or substituted indigo by reducing the hydrochloride with zinc and glacial acetic acid. D. B.

**Quinoline and Pyridine Compounds.** (*Dingl. polyt. J.*, **252**, 123—126.)—Jacobsen states that for the preparation of yellow dye-stuffs from pyridine and quinoline bases the phthalic anhydride may be replaced by chlorinated phthalic acids. The yellow dye obtained

by the action of phthalic acid on the coal-tar bases boiling at 235—240° is identical in properties and composition with that obtained from quinaldine and phthalic acid. The same dye is formed from methylquinoline obtained by the reduction of orthonitrobenzylidenacetone. Yellow dyes are obtained also by converting cumidine into cumoquinaldine or trimethylquinaldine by treatment with aldehyde and hydrochloric acid, and heating with phthalic anhydride, phthalimide, nitrophthalic acid, or chlorinated phthalic acids.

Pure quinoline does not form a yellow dye with phthalic acid. Yellow dyes are obtained, however, by methylating (ethylating, amylating, &c.) quinoline and treating the product with phthalic anhydride or substituted phthalic acids.

For the preparation of hydroxyquinolines, the Farbwerke treats sulphonic acids of primary aromatic amines with glycerol and sulphuric acid, and adds aromatic nitro-compounds.

Knorr obtains quinoline derivatives, whose pyridine nucleus is hydroxylated, from ethyl acetoacetate and its alkyl and halogen substitution products on the one hand, and aromatic monamines (aniline, toluidine, xylydine, cumidine, naphthylamine, amidoanthracene, amidobenzoic acid, or their alkyl or halogen substitution products, chlorine, bromine, iodine, methyl, ethyl derivatives, as well as their azo-derivatives) on the other hand, by heating them in equivalent quantities at 120° for several hours and treating with sulphuric acid.

Ladenburg and Roth show that the piperidine prepared from pyridine by synthesis is identical with the base obtained from pepper.

Königs and Geigy describe the preparation of hydroxypyridine-carboxylic acid from hydroxyquinolinic acid as well as the formation of pyridinedisulphonic acid, by heating piperidine with concentrated sulphuric acid. On treating this with phosphorus pentachloride, trichloropyridine is obtained.

D. B.

**Preparation of Anthraquinone Compounds.** By H. ENGELSING (*Dingl. polyt. J.*, **252**, 183).—On heating 1 part anthraquinone-sulphonic acid with 2 parts fuming nitric acid and 3 parts sulphuric acid, the temperature rises rapidly towards the completion of nitration, and sulphurous anhydride is evolved; as soon as this ceases, the mixture is heated for 10—15 minutes at 180—185°. The resulting mass consists of a red and blue colouring-matter, the red being more soluble in alcohol than the blue. The blue dye is readily soluble in water, and forms blue salts with bases (basic and normal), the red dye forming red normal and blue basic salts. Both dyes are fixed by mordanted vegetable fibres.

D. B.

**Preparation of Ammonium Albuminate.** By E. MUTH (*Dingl. polyt. J.*, **252**, 86).—The author uses a compound of casein with ammonia—called ammonium albuminate—as a substitute for ordinary paper size. He mixes 100 kilos. dry casein with 10 kilos. pulverised ammonium carbonate and 1 kilo. ammonium phosphate until the mixture assumes a uniform appearance and pale yellow colour. The reaction is completed in from 15—20 hours.

D. B.

**Composition of Turkey-red Oil and its Mode of Action.** By A. MÜLLER-JACOBS (*Dingl. polyt. J.*, **251**, 499—506, and 547—552).—The following is a summary of the researches which form the subject of this paper. Turkey-red oil is a saturated solution both of unaltered oil (triglyceride), and of decomposition products of sulpholeic acid in the alkali salts of this or an analogous acid, *e.g.*, sulphoricinoleic acid. It acts as a mordant, inasmuch as it gives up its oil in a finely divided form to the fibre. In the process which gives the best results, the sulpholeates are removed as much as possible by means of washing, whilst in the less complicated processes the property possessed by sulpholeic acid—to form insoluble salts with aluminium hydroxide—is simultaneously utilised for the fixation of the mordant. The preference given to the product from castor-oil depends on the presence of a larger amount of oil in the corresponding sulpholeic acid, so that such Turkey-red oil gives up a greater proportion of oil to the fibre than the analogous products of other triglycerides. It is evident, therefore, that the “new process” which has revolutionised Turkey-red dyeing could not have been discovered until the most suitable conditions for preparing this product had been fully and completely attained. The experiments made by Runge, Mercer, and Greenwood, as well as those of Keyser, failed owing to the fact that the methods which they adopted for obtaining the mordant were accompanied by the evolution of sulphurous anhydride. The so-called “Acide sulfoleique” mordant used for the fixation of aniline dyes also made but little progress, since the characteristic feature of a Turkey-red oil, *i.e.*, complete solution in water of a definite amount of an unaltered oil was disregarded in its preparation.

In 1873 the author published the results of some experiments made with a view to simplify the Turkey-red mordanting process, based on the conversion of the triglycerides into a finely divided emulsion by the addition of a solution of gum and an alkaline hypochlorite. The experiments were very successful, as by the use of the resulting mordant once passing replaced the usual oft-repeated soap-baths, a bright and permanent colour being obtained. Subsequently, the author took out a patent for the preparation of a mordant known in commerce under the name of Turkey-red oil, and in his specification he described minutely the conditions required for the successful preparation of a mordant. Thus far, the author claims a share in the “new Turkey-red process.”  
D. B.

**Tincture of Nux-Vomica.** By M. CONROY (*Pharm. J.* [3], **14**, 461—462).—In order to study the effect of alcohol of various strengths on nux-vomica, several lots of the same sample of finely-powdered nux-vomica were extracted by the British Pharmacopœia process with alcohol of different strengths: (1) proof spirit; (2) a mixture of half proof and half rectified spirit; (3) rectified spirit as recommended in the British Pharmacopœia; (4) stronger rectified spirit; (5) a mixture of equal parts of absolute alcohol and rectified spirit; (6) absolute alcohol. The table given below shows the specific gravities of these menstrua, and the results of the analysis, &c., of the tincture:—

No. of experiment.	Specific gravity of menstruum at 60° F.	Specific gravity of tincture at 60° F.	Per cent. dry extract from tincture.	Total alkaloids per cent.	Strychnine, per cent.	Brucine, per cent.
1	0·920	0·924	1·353	0·209	0·083	0·126
2	0·882	0·886	1·320	0·209	0·084	0·125
3	0·838	0·842	1·056	0·190	0·077	0·113
4	0·830	0·834	0·957	0·119	0·045	0·074
5	0·820	0·823	0·803	0·081	0·030	0·051
6	0·795	0·798	0·748	0·032	—	—

From these results, it is evident that the rectified spirit of the Pharmacopœia, and alcohols of greater strength, are unsuitable as menstrua for the extraction of nux-vomica; the reason is that the strong spirit hardens the cell-walls, by coagulating albumin and absorbing water, and therefore impedes osmotic action, whereas dilute spirit softens the cell-walls, causing them to swell up, promotes osmose, and consequently solution. The best menstruum is No. 2 spirit (sp. gr. 0·882).

D. A. L.

**Purgative Principle of Croton-oil.** By H. SENIER (*Pharm. J.* [3], 14, 446).—By means of alcohol, commercial croton-oil may be separated into two portions, one soluble, the other insoluble in this medium (this vol., p. 909); the former contains the vesicating principle, whilst the latter is non-vesicating, and constitutes the purgative principle which may be obtained, therefore, by simply washing croton-oil with alcohol until nothing more is dissolved. It is administered in the form of pills with extract of hyoscyamus. In doses equivalent to the non-vesicating oil in  $\frac{1}{10}$  minim of ordinary croton-oil, it gives rise to slight nausea, uncomfortable sensation, but no appreciable effect; in doses equivalent to the amount of this oil in a half minim of ordinary croton-oil it acts as a very powerful purgative. The vesicating principle irritates the alimentary canal, gives rise to nausea, but does not purge.

D. A. L.

**Spontaneous Decomposition of "Explosive Gelatin."** By C. E. MUNROE (*Chem. News*, 49, 259).—A sample of camphorated explosive gelatin was wrapped in paraffin-paper, and this parcel in light brown paper. After some time, more than a year, the volume had diminished considerably, nitrous fumes were evolved, and had attacked the paper, whilst clusters of fine crystals were found on the outside of the paper. The mass was friable, and after a short immersion in water disintegrated; and the camphor odour, which was quite strong up to this stage, soon disappeared. The water was straw coloured, gave a strongly acid reaction, contained traces of nitrous (but no nitric) acid along with oxalic acid, and a sugar-like substance giving



glucose reaction with Fehling's solution. The paraffin remained unchanged, but neither glycerol, nitroglycerol, nor gun-cotton could be detected.

D. A. L.

**Experiments with Compressed Gun-cotton.** By W. v. FÖRSTER (*Dingl. polyt. J.*, **251**, 371—373).—In replying to a criticism by O. Guttman, the author states that he is able to determine how far his experiments in which the explosion took place in an open space are of use as a basis of inferring what took place in a confined space. He is of opinion that the experiments hitherto made and the theories hitherto advanced, do not fully explain this point, and although his experiments do not completely develop the theory of explosion, they establish additional principles. His process for rendering gun-cotton and gun-cotton cartridges waterproof is effective, inasmuch as gun-cotton which has hitherto been considered insoluble is dissolved, and forms the coating of the substance itself. He is aware that points of entrance are left open to the water, and to make the surfaces perfectly impervious to water he varnishes the pieces of gun-cotton after treatment, with acetic ether. In regard to the spontaneous decomposition of gun-cotton, the author states that gun-cotton even when badly prepared under ordinary conditions, will not decompose with production of fire or even explosion.

D. B.

**Three Processes for Obtaining the Albuminoid Matter from Potato Waste.** By W. KETTE (*Bied. Centr.*, 1884, 172—174).—A considerable amount of albuminoid matter is contained in the liquid from which the potato-starch has separated; to recover this, and to use it as fodder, 12 to 14 litres of sulphuric acid is added to 45,000 litres of liquid, or 4 litres sodium silicate solution mixed with 12 litres sulphuric acid, or else acid dextrin solution; this is prepared from the waste pulp in the cylinders, 102 litres of this pulp (which contain about 6 kilos. starch) are mixed with 9 litres acid and 34 litres water, and the whole is heated with steam in a large vessel. The author proceeds with the description of the apparatus employed, and states that the precipitate so obtained, after neutralisation with soda, may be given to cattle, and although it contains sodium sulphate, no unpleasant effects have been observed. When dried, the mass contains over 40 per cent. of albuminoids, and about 0.4 per cent. fat.

E. W. P.

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## General and Physical Chemistry.

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**A Mercury Galvanometer.** By J. CARPENTIER (*Compt. rend.*, **98**, 1376—1377).—In 1881 the author made experiments similar to those described by Lippmann (this vol., p. 881), and constructed a galvanometer on the same principle. C. H. B.

**A Mercurial Electrodynamometer.** By G. LIPPMANN (*Compt. rend.*, **98**, 1534—1535).—A small parallelepipedal chamber, filled with mercury and communicating laterally with the two branches of a manometer, is supported in the centre of a bobbin of copper wire. The current passes through the wire and then through the mercury, and the manometer shows a permanent deviation due to the electrodynamic action exerted on the mercury by the remainder of the circuit. The deviation is strictly proportional to the square of the intensity of the current, and the apparatus can be used to measure alternating currents. All the parts of the apparatus are rigid and immovable with the exception of the mercury, and even in this latter case the points at which the current enters and leaves the mercury have an invariable position with respect to the rest of the apparatus. In consequence of this rigidity, the form and sensibility of the apparatus remain perfectly constant.

This instrument can be constructed to measure currents in absolute measure, for the pressure  $p$  indicated by the manometer is connected with the intensity  $I$  by the formula

$$p = \frac{C}{E} I^2.$$

where  $E$  is the thickness of the layer of mercury and  $C$  is the intensity of the magnetic field produced at the centre of the bobbin by a current of unit intensity. The former is measured directly; the latter is deduced from the dimensions of the bobbin and increases indefinitely with the number of turns of the copper wire. In the mercurial galvanometer (this vol., p. 881) both the numerator and denominator in the expression  $\frac{H}{E}$  have a maximum limit. The author criticises Carpentier's note (preceding Abstract). C. H. B.

**Heat liberated by the Compression of Solid Bodies.** By W. SPRING (*Ber.*, **17**, 1215—1217).—Jannettaz states (*Ber.*, **17**, 98) that a block of bell-metal subjected to a pressure of 6000 atmospheres showed signs of melting on its surface, and inferred from this that a considerable liberation of heat had been caused by the pressure. Spring has subjected acephorone (m. p. 28°) and also azoxybenzene (m. p. 36°) to a pressure of 7000 atmospheres, but in neither case has the least sign of fusion been apparent. In order to prove

that no local heating takes place, he substituted gunpowder for these substances, so that any local heating would cause the ignition of the whole mass: no ignition took place. The author believes the effect observed by Jannettaz to be due to friction. In Jannettaz's experiments, the metal was pressed between two plates, so that lateral motion (with friction) was possible; whereas Spring's experiments were conducted with a closed pressure chamber, thus preventing any lateral movement.

L. T. T.

**Relation between Molecular Weight and Velocity of Evaporation of Liquids.** By C. SCHALL (*Ber.*, 17, 1044—1058).—In a former paper (this vol., p. 551) the author states that the time of evaporation of equal weights of liquids, each heated in its own vapour, is inversely proportional to their molecular weights; or that quantities by weight of different liquids proportional to their molecular weight, when heated in their own vapours, evaporate equally quickly; or lastly, that equal weights of two substances, when heated in their own vapours, evolve quantities of vapour which, when sufficiently heated, occupy, according to Avogadro's law, equal spaces in equal times. A complete description of the complicated apparatus, by means of which these propositions were proved, is given in this paper, and also an account of a large number of estimations. Eleven substances have been tried, and if the time of evaporation of benzene be taken at 1, the time of evaporation of equal volumes of vapour (which represents quantities in proportion to the molecular weight) is as follows:—

Sulphide of carbon = 1.00	Tetrachloride of carbon = 0.945
Ether ..... = 0.99	Ethyl acetate ..... = 0.98
Ethyl bromide.... = 0.97	Acetone ..... = 0.99
Chloroform ..... = 0.94	Methyl alcohol ..... = 1.00
Ethyl iodide..... = 0.98	Water ..... = 1.00

A. B.

**Dependence of Boiling Point on Pressure.** By G. W. A. KAHLBAUM (*Ber.*, 17, 1245—1262; and 1263—1272).—These papers are in continuation of the author's earlier communication on this subject (this vol., 141), and give the results of the careful examination of about 50 compounds. The influence on the resultant numbers due to error of experiment is believed not to exceed 0.001 in the case of the specific remission,\* and 1.5° in the case of boiling points.

A comparison of the results obtained leads to the general law that at 0 mm., "the specific remission and also the reduction in boiling point vary in direct proportion to the boiling point;" or, in other words, the specific remission and reduction in boiling point in homologous compounds vary with the introduction of  $\text{CH}_2$  in a manner similar to that in which the boiling point varies. This law has a special interest, as likely to be of service in determining the constitution of a substance and the size of its molecules. For—as the

\* Specific remission (sp. r.) is the relation of the reduction in boiling point to the reduction in pressure.

change of boiling point is caused by the reduction in pressure—the different reduction in boiling point of various compounds for the same reduction of pressure shows that the pressure on each molecule of one liquid, caused by the pressure of the air, is different from that on each molecule of another liquid. But since the *absolute* reduction in pressure is the same in both cases, the different reduction in boiling point would appear to be due to the different size of the single molecules in the two liquids; and therefore the difference in the reduction of temperature for the same reduction of pressure would be a measure of the relative size of the molecules.

In homologous series, the average numerical results obtained are, that a variation in composition of  $\text{CH}_2$  causes a variation in specific remission of 0.01, and in the reduction of boiling point of  $7.6^\circ$  for 0 mm. pressure. These numbers agree with the observations in 17 cases, but disagree in 3 cases, but the author is not prepared at present to regard these numbers as having more than a subordinate signification.

Attention is called to the fact that the difference in boiling point between various substances is less at a low pressure than at the ordinary pressure of the air. The reputed fact that different substances are more easily separated by fractional distillation under low than under ordinary pressures, cannot have its origin in the boiling points lying further apart in the former than in the latter case; but, if really a fact, must be due to some entirely different cause.

In the numbers obtained certain regularities are, as already said, to be observed, but still there are many irregularities. And this was to be expected, for we may express the equation for the boiling point of a substance as

$$S = C + A + D + O + H + Z,$$

where C is the cohesion, A the adhesion, D the pressure of air and vapour, O the surface tension, H the pressure of liquid on itself, and Z the increase of cohesion caused by D, O, and H. In every case, boiling will commence when the heat given to the liquid exceeds the value of S. In the present case, therefore, it is only one of the elements determining the boiling point which has been eliminated, and that the simplest one. It is thus clear that most, if not all, the irregularities to be observed at ordinary pressures will still be observed at 0 mm. pressure, and many perhaps in a more marked degree. Probably the most important of the elements of the above equation beyond D are C and A. The results obtained by other investigators show that adhesion does influence the boiling point, and that it varies with the material composing the boiling vessel; but little is at present known as to the extent of such influence. It would however appear that it is the cohesion of the liquid which chiefly determines the boiling point when the pressure is removed, and tends to hinder the change of aggregation from the liquid to the gaseous state.

A generally accepted definition of boiling point is "the temperature at which the vapour tension of the liquid is sufficient to counter-balance the pressure of the air." But the author shows that this definition of boiling point is quite wrong, as the effect of cohesion in

hindering change of aggregation is entirely omitted. The tension of the molecules given off from the surface of a liquid is sufficient to counterbalance the pressure of the air, at a temperature decidedly below that necessary for entirely overcoming the cohesion. This is shown to be experimentally true by a comparison of the author's numbers with those of Landolt. Landolt determined the vapour tension; the author the actual boiling point; and in each case his numbers were higher, in many cases very considerably higher, than those obtained by Landolt. The author defines as boiling point "the temperature of the vapour of a liquid in motion at which all its molecules pass from the liquid to the gaseous state without change of pressure."

L. T. T.

**Dissociation of Salts containing Water and Relation of the Dissociation to the Molecular Volume of the Combined Water.** By W. MÜLLER-ERZBACH (*Ber.*, 17, 1417—1421).—In these experiments, the vapour-tension of the water in the salt is compared with that of pure water; the ratio of these tensions gives a measure of the energy with which the water is held in combination in the salt. In many cases the tension diminishes after a portion of the water is lost, *e.g.*, sodium phosphate,  $\text{Na}_2\text{PO}_4 + 12\text{H}_2\text{O}$ , tension ratio at  $17^\circ = 0.67$ ; after loss of 25 per cent. of water, tension ratio at  $16^\circ = 0.30$ . The vapour-tension appears to decrease with a decreased molecular volume for the water in the salt: for instance, with three salts containing 10 molecules of water of crystallisation:— $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ , mol. vol. of water = 16.7, tension ratio = 0.78;  $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$ , mol. vol. of water = 15.2, tension ratio = 0.67;  $\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$ , mol. vol. of water = 14.8 to 13.2, tension ratio = 0.28. A. J. G.

**General Law of Freezing of Solvents, and Deductions therefrom.** By F. M. RAOULT (*Ann. Chim. Phys.* [6], 2, 66—125).—In this extensive memoir are collected together the results obtained in an investigation on the lowering of the freezing point of liquids by the solution in them of various substances; the sources of experimental error are also discussed, and deductions drawn from the results as to the determination of molecular weights, and the subdivision of a base between two acids (comp. Abstr., 1880, 523; 1882, 1260; 1883, 7, 278, 952).

**PART I. Experimental.**—If A represent the *coefficient of lowering*, *i.e.*, the lowering of freezing point produced by 1 gram of substance dissolved in 100 grams of solvent, M the molecular weight of substance dissolved, and T the *molecular lowering of freezing point*, *i.e.*, the lowering of freezing point produced by the solution of 1 molecule of substance dissolved, then  $MA = T$ . Practically it is found advisable to experiment with very dilute solutions in order to avoid errors arising from arbitrary evaluations of the water of crystallisation or combination of the substance dissolved. The solvents employed were water, benzene, nitrobenzene, ethylene dibromide, acetic and formic acids. The method of experiment consisted, in outline, of determining the freezing point of the solvent with and without the substance dissolved within a short interval of time. If P be the weight of the solvent,

P' that of the substance dissolved, K the lowering of the freezing point, then the coefficient  $A = K \frac{P}{P' \times 100}$ . The liquid is cooled, while constantly stirred, to about  $\frac{1}{4}^{\circ}$  below the freezing point. The thermometer quickly rises, and then remains stationary at a certain point for a short time. This point is taken to be the freezing point. The magnitude of errors due to reading the thermometer scale, radiation, incomplete immersion of the stem of the thermometer, displacement of zero point, and alteration in the liquid during the experiments, are fully discussed. The conditions necessary in order to obtain comparable results are also carefully examined.

The conclusions arrived at, illustrated by a selection of examples in the memoir, are given below.

(1.) All substances, solid, liquid, or gaseous, when dissolved in a liquid which can be solidified, lower the point of solidification.

(2.) In the case of the solvents examined, the molecular lowering of freezing point, due to the solution of different substances, approximates to one of two values, one of which is double the other; these vary with the nature of the solvent.

These mean values are 117 and 58 for ethylene dibromide, 72 and 36 for nitrobenzene, 49 and 24 for benzene, 39 and 18 for acetic acid, 28 and 14 for formic acid, 47—37 and 18.5 for water. The higher of each of these pairs of values is the more common, and is designated by the author the *normal* value, and the lower the *abnormal* value.

#### EXAMPLES.

Solvent.	Substance dissolved.	Molecular weight.	Coefficient A.	Molecular coefficient T = M A.
Acetic acid	Methyl iodide....	142	0.273	38.8
" "	Naphthalene ....	128	0.306	39.2
" "	Formic acid ....	46	0.793	36.5
" "	Sulphuric acid ..	98	0.189	18.6
" "	Hydrochloric acid	36.5	0.471	17.2
Benzene	Methyl iodide....	142	0.335	50.4
"	Naphthalene ....	128	0.391	50.0
"	Ethyl formate ..	74	0.666	49.3
"	Methyl alcohol ..	32	0.791	25.3
"	Formic acid ....	46	0.504	23.2
Water	Hydrochloric acid	36.5	1.071	39.1
"	Ammonium sul- phate, potassium chromate, sul- phate and carbo- nate .....	—		38.0

These results will serve as a means for fixing the molecular weight of a substance, for if A is determined experimentally, then in the case of water T = 38 divided by A will give the molecular weight.

It is further shown that in a constant weight of a given solvent, every molecule, of whatever nature it may be, produces the same

lowering of freezing point. For example, if the higher of the two values for T given above are divided by M, the molecular weight of the solvent, then the quotients are, with the exception of water, practically equal.

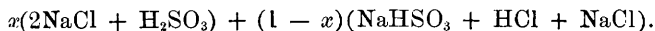
Solvent.	Molecular weight M.	Maximum value for T.	M + T.
Water.....	18	47	2.61
Formic acid .....	46	29	0.63
Acetic acid.....	60	39	0.65
Benzene .....	78	50	0.64
Nitrobenzene .....	123	73	0.59
Ethylene dibromide	188	119	0.63

It would appear that the molecule of liquid water does not consist of isolated chemical molecules of the simple formula  $H_2O$ , but probably of four such molecules combined or condensed together. From the results in the table above, the general law of the freezing of solvents may be enunciated as follows:—

(1.) *If a molecule of any kind be dissolved in 100 molecules of a liquid of a different kind, there is produced a lowering of freezing point of the solvent approximately equal to 63. Consequently the lowering of freezing point of a dilute solution is approximately equal to the product obtained by multiplying 63 by the ratio existing between the number of molecules dissolved and the molecules of the solvent.*

PART II. *Deductions.*—It is remarkable that the acids, as regards the effect produced by them on the lowering of the freezing point of water, are separable into two groups; the value for T of members of one group is approximately 40, of the other 20. The members of the former group are powerful acids, whilst those of the latter are the weaker acids. It is here shown that *equivalents of the acids of the first group displace almost completely equivalents of the acids of the second group from their combinations with bases.* To illustrate this proposition, examples are given, such as the action of hydrochloric acid on neutral sodium sulphite, nitric acid on sodium iodate, sulphuric acid on sodium arsenite, hydrochloric acid on potassium arsenate, the first of which may be taken in order to show the method used.

If by  $x$  be denoted the fraction of the molecule of sulphurous acid liberated by the action of 2 molecules of hydrochloric acid on 1 molecule of sodium sulphite, then at the end of the change the composition of the mixture may be represented by the formula—



The lowering of freezing point due to each of the components of the above formula is as follows:—

A.	1 molecule	NaCl in 2 litres water.....	1.7
B.	1	" $H_2SO_3$ " " .....	0.955
C.	1	" $NaHSO_3$ " " .....	1.62
D.	1	" HCl in 2 litres water.....	1.835
E.	1	" $Na_2SO_3$ " " .....	2.105

The liquid obtained by mixing solution D with half E causes a

lowering of freezing point of 1.472, or referred to the same standard of 2 litres =  $1.472 \times 3 = 4.416$ ; hence

$$x(2 + 1.7 + 0.955) + (1 - x)(1.62 + 1.835 + 1.7) = 4.416$$

$$\text{or } x = 0.958.$$

i.e.,  $\frac{95.8}{100.0}$  of the sulphurous acid are liberated by the action of the hydrochloric acid. The results in this memoir are in accordance with those obtained by Berthelot in his thermochemical investigations, and point to a correlation between the lowering of the freezing point and the chemical energy of the acids. Similarly it is shown that the bases can be separated into two groups. The value for T of members of one group varies between 33 and 48, mean 39, and for the other group the value varies from 16 to 20, mean 19. Included in the first group are the hydroxides of the metals of the alkali and alkaline earth groups, together with those of tetramethyl- and trimethylethylammonium, while in the second group are the organic bases, together with ammonia. As in the case of the acids, so also it is shown that the members of the first group completely eliminate the members of the second group from their combination with acids. The results are strictly in accordance with the observations of Berthelot, that ammonia and aniline are completely displaced by soda, and with those of Menshutkin, that ammonia and the organic bases are displaced by soda in alcoholic solution.

Examples are given to illustrate the action of the hydroxides of barium and rubidium on ammonium chloride, and of trimethylethylammonium hydroxide on ammonium iodide. There is thus a similar correlation to that observed in the case of acids between the lowering of the freezing point and the chemical energy of the bases.

In conclusion, the author traces out an analogy existing between the phenomenon of the lowering of the freezing point and that of the heat of dilutions of the acids and bases. This may be stated generally thus: those acids and bases which lower the freezing point of the solvent to the greater degree possess the greater affinity for that solvent. It is proposed to illustrate this analogy in a future memoir.

V. H. V.

**Displacement of Chlorine by Bromine, and Reactions accompanied by the Absorption of Heat.** By A. POTILITZIN (*Ber.*, 17, 1308—1324).—The author has previously shown (*Abstr.*, 1882, 457) that the displacement of chlorine in metallic chlorides by bromine takes place according to a simple rule, which may be expressed by the equation  $\frac{A}{BE^2} = \text{Const.}$ , where A is the atomic weight of the metal, B the percentage of chlorine displaced, and E the valency of the metal. The correctness of this equation has been confirmed by the results of the examination by the author of the action of bromine on the chlorides of 14 metals, whose valency varied between 1 and 6, and atomic weights between 7 and 207. Amongst these were cobalt and nickel, which, having equal valencies and atomic weights, formed good examples to test the correctness of the law.



The author disputes the soundness of the arguments used by Berthelot (Abstr., 1883, 8) to show that this displacement of chlorine by bromine may be fully explained according to his "*principe du travail maximum*," and denies the possibility of the existence, under the conditions of the experiments, of the perbromides and bromine chloride, the formation of which Berthelot assumes. The author considers that this reaction must be classed amongst those reactions which take place at certain temperatures, notwithstanding that they are accompanied with an absorption of heat, and that the work of chemical change in these cases is completed at the expense of the heat of the surrounding medium. He believes that the real cause of the reaction must be sought in intramolecular conditions, and is probably due to the varying velocity of the molecules, in accordance with Clausius' generally received theory.

The author has repeated the experiments with silver, potassium, and sodium chlorides at ordinary temperatures, and is unable to confirm Berthelot's results. He finds that there is a very slight displacement of chlorine in silver chloride (about 0.8 per cent. after six days' treatment), that with potassium chloride the displacement is much less (less than 0.1 per cent.), and with sodium chloride is scarcely perceptible.

L. T. T.

**Vapour-density Apparatus.** By V. MEYER (*Ber.*, 17, 1334—1335).—The author disputes the advantages (except perhaps in special cases) claimed by Schwarz (Abstr., 1883, 899) for his modification of the author's apparatus. In such an apparatus, the neck should be as small (to hinder diffusion), the gas space as large as possible. The unheated portion should be small, and the vertical position of the apparatus is to be preferred so as to minimize diffusion. Finally, it is important to have a constant temperature, and for easily decomposable substances it is advantageous to know that temperature. The author contends that these conditions are not so completely fulfilled in Schwarz's apparatus as in his own.

L. T. T.

**Specific Volume of some Double Chlorides.** By R. ROMANIS (*Chem. News*, 49, 273).—The author has observed that a great contraction takes place in the specific volumes of some anhydrous double chlorides. For example, the sp. vol. of ammonium platinochloride,  $(\text{NH}_4)_2\text{PtCl}_6$ , is 148, and that of  $\text{PtCl}_4$  being 114.7, and of  $2(\text{NH}_4)\text{Cl}$  71.32, there is a contraction equal to 38. A similar contraction is observed with the platinochlorides of zinc, cobalt, nickel, &c., whilst the contraction in the case of potassium platinochloride amounts to 54.5. The stannochlorides behave in a similar manner, e.g., potassium stannochloride,  $\text{K}_2\text{SnCl}_6$ , sp. gr. is 2.948, and sp. vol. 138.6, the contraction being 52.5; ammonium stannochloride,  $(\text{NH}_4)_2\text{SnCl}_6$ , sp. gr. = 2.511 and sp. vol. 146.1, contraction = 39.8. On the other hand, combinations of  $\text{PtCl}_2$ ,  $\text{ZnCl}_2$ , and  $\text{SnCl}_2$  exhibit an expansion, e.g.,  $(\text{NH}_4)_2\text{PtCl}_4$ , sp. gr. = 2.84, sp. vol. = 132, and sum of sp. vols. of  $\text{PtCl}_2$  and  $2\text{NH}_4\text{Cl}$  = 116.8;  $(\text{NH}_4)_2\text{ZnCl}_4$ , sp. gr. = 1.77, sp. vol. = 137, expansion = 17. Sp. vol. of  $\text{K}_2\text{SnCl}_4$  = 136.6. As an example of a trichloride,  $\text{K}_3\text{S}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ , sp. gr. = 2.42, sp. vol. = 200.8.

D. A. L.

**Spheroidal State.** By J. LUVINI (*Compt. rend.*, **98**, 1536).—Water boils at  $-18^{\circ}$  to  $-20^{\circ}$  under a pressure of 1 mm., and the temperature of water in the spheroidal state under this pressure must be less than  $-18^{\circ}$ . It is easy to see, therefore, that the temperature of very volatile liquids in the spheroidal state under very low pressures must be very low. In Despretz's experiment with nitrous oxide in the spheroidal state, under a pressure of 20 mm., the temperature of the nitrous oxide must have been below  $-200^{\circ}$ .

A platinum capsule previously heated in boiling water was placed on a hot brick, and 13—15 c.c. of ether poured into it. A tube containing water was placed in the ether, a receiver placed over the whole, and the pressure reduced to 100—120 mm. The water froze in about one minute. Under a pressure of 6—7 mm., water could be frozen in alcohol, and at 8—10 mm. mercury can be frozen in ether.

C. H. B.

**Colloïds.** By E. GRIMAUX (*Compt. rend.*, **98**, 1434—1437).—*Schweizer's Solution.*—When the solution obtained by the action of ammonia on copper turnings is dialysed in a porous vessel, ammonio-copper nitrite and the excess of ammonia pass through, and after six or seven days the porous vessel contains a blue solution of ammonio-cupric oxide, which will not pass through the dialyser. This solution has properties similar to those of other colloïds. It yields a gelatinous precipitate of cupric hydroxide on the addition of water, decomposition being partial with 1—2 vols. of water, and complete with 5—6 vols., and it is also precipitated by magnesium, calcium, aluminium, and copper sulphates, and by dilute acetic acid, but not by sodium chloride or potassium sulphate. When the solution is heated to  $40-50^{\circ}$ , it yields a precipitate of cupric hydroxide, which redissolves on cooling, the action of heat causing true dissociation. When a solution of cellulose in Schweizer's reagent is dialysed, the liquid left in the dialyser is much less highly coloured than the original solution. It yields a gelatinous precipitate of cellulose when mixed with water, but this precipitate is dissolved on adding a few drops of ammonia, and yields a perfectly transparent and but slightly coloured solution. If dialysis is carried too far, the solution is decomposed, and a firm deep blue jelly forms in the dialyser, and can be freed from mother-liquor by washing with water. This jelly consists of cellulose and cupric oxide, and is not soluble as a whole in ammonia; the latter dissolves out the cupric oxide from it.

*Pyruvic Ureïdes.*—The solutions obtained by dissolving in alkalis the white powders which are formed when crystallised pyruvic ureïdes are heated at  $150^{\circ}$ , have the properties of other colloïdal solutions, and yield a precipitate when treated with a current of carbonic anhydride, but become limpid again when treated with a current of air. They differ, however, from the colloïds of the animal organism by the fact that they are not affected by boiling nitric acid.

*Amido-aspartic Colloïd.*—This substance is obtained by heating aspartic anhydride with urea at  $125^{\circ}$ , or by the action of a current of ammonia-gas on aspartic anhydride at  $150^{\circ}$ . Its solution gelatinises on evaporation, and yields bulky precipitates with baryta-water,

calcium chloride, &c. The precipitate formed by nitric acid dissolves on heating, and is reprecipitated on adding water. Sodium chloride produces only a slight precipitate in the cold, but an abundant precipitate on heating. The precipitate produced by magnesium sulphate is dissolved on gently heating, but is permanently reprecipitated on boiling.

This colloïd readily undergoes hydration, yielding a non-colloïdal substance; with copper salts this forms a derivative, which dissolves in potash and produces a rose-violet solution exactly similar to that of the analogous derivatives of albuminoids.

*Soluble silica* is easily obtained by boiling 8 grams of methyl silicate with 200 grams of water in a flask provided with an inverted condenser. The liquid is evaporated to three-fourths of its bulk in order to expel methyl alcohol, and the solution thus obtained contains 2.26 per cent. of anhydrous silica. It is very stable, and is not coagulated by the action of carbonic anhydride even on heating, but is precipitated by a somewhat large quantity of sodium chloride or potassium sulphate at 100°. The properties of the solution agree with those previously described by Graham.

C. H. B.

**Simple Method of Demonstrating Spring's Compression Experiments.** By B. TOLLENS (*Ber.*, 17, 662—664).—The author employs the press on the knee-joint principle already described by him (*Ber.*, 9, 488). His results in general confirm those already described by Spring. Potato-starch gave a cylinder, in part transparent, in part opaque. In the transparent parts starch granules could no longer be recognised under the microscope.

A. J. G.

**History of the Periodic Law.** By J. A. NEWLANDS (*Ber.*, 17, 1145—1150).—A question of priority.

**Mixed Crystallisation.** By H. KOPP (*Ber.*, 17, 1105—1121).—The author criticises Brügelmann's statement (*Chem. Centr.*, 1882, 522; 1883, Nos. 30—32; and this Journal, Abstracts, 1883, 147—148) "that compounds of dissimilar atomic constitution can assume the same crystalline form, and that such compounds crystallise together in varying proportions."

In a series of experiments on the crystallisation of mixed salts, in which small quantities of the saturated solutions were allowed to crystallise on watch-glasses coated with a thin film of paraffin, it was observed that the salts of dissimilar constitution crystallised separately. When a solution of potassium nitrate with permanganate, chromate, or dichromate crystallises, the crystals of potassium nitrate which are deposited are coloured by the small quantities of chromate or permanganate contained in the cavities in which these crystals abound. Potassium chloride and sulphate also exhibit these cavities, and consequently behave in a similar manner. The chromate or permanganate is only mechanically enclosed in these crystals, and their presence cannot be regarded as a proof that these salts of dissimilar constitution crystallise together.

W. C. W.

**Influence of Repeated Compression on the Amount of Sulphides formed by Pressure.** By W. SPRING (*Ber.*, 17, 1218—1220).

—The author subjected the mixtures of metals and sulphur to repeated compressions, the block obtained being powdered between each two applications of pressure. The following results were obtained:—

	One compression.	Two compressions.	Four compressions.	Six compressions.
Silver sulphide .....	4·51 p.c.	12·43 p.c.	46·74 p.c.	69·41 p.c.
Lead „ .....	1·32 „	19·34 „	28·08 „	45·54 „
{ Cuprous sulphide* ....	14·09 „	28·20 „	40·08 „	56·89 „
{ Cupric „ ....	8·49 „	16·95 „	24·02 „	34·60 „

The mere powdering also slightly increases the amount of sulphide formed. Time plays an important part in the completion of the reaction. A block of silver and sulphur, which had twice been subjected to pressure, and contained 12·43 per cent. silver sulphide, was re-analysed after an interval of a year, and was then found to contain 41·63 per cent. of sulphide. These experiments therefore show that the amount of sulphide formed depends on the degree of pressure, the amount of surface contact of the two constituents, and the time during which such contact lasts.

L. T. T.

## Inorganic Chemistry.

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**Action of Sulphur on Oxides.** By E. FILHOL and SENDERENS (*J. Pharm.* [5], 7, 480—482).—Sulphur acts on potassium and sodium hydroxide, even at normal temperatures, forming polysulphide and thiosulphate. When sulphur is mixed with aqueous solutions of potash or soda, the chemical action is inversely as the quantity of water present, and directly as the temperature. A solution containing 200 grams of sodium oxide in a litre of water was acted on by sulphur at the normal temperature; the reaction was complete in 24 hours. When the quantity of sodium oxide was reduced to 40 grams per litre, the reaction commenced after about 20 hours, but was not completed after one month. Heating the solution at 100° very much hastened the reaction, which was then complete in a few hours. A solution containing 4 grams of sodium oxide per litre was not sensibly acted on by sulphur, even after many months, but the reaction takes place when the solution is heated at 100°. A solution of sodium oxide containing 0.4 gram per litre of water was not acted on by sulphur, either at ordinary temperatures or when heated. These observations

\* The author is uncertain whether the copper is present in the cupric or cuprous state, or in both.

are strictly in accordance with the laws of thermo-chemistry. The calculations in the original paper indicate that whilst the heat of combination of sodium oxide in the solid state is 152 cals., the heat of formation of sodium tetrasulphide and thiosulphate, also in the solid state, is 224.1, that is 72 cals. in favour of the second reaction. On the other hand, the thermo-chemical equivalents of the same bodies when dissolved in water are 232.8 cals. in the first reaction, and 232.9 cals. in the second, that is, the two reactions are thermo-chemically identical.

W. R. D.

**Solubilities of Haloïd Salts.** By A. ÉTARD (*Compt. rend.*, 98, 1432—1434).—*Sodium Bromide*.—The author's results agree with those of Kremers. Between  $-20^{\circ}$  and  $+40^{\circ}$  the solubility is given by the equation  $S = 40 + 0.1746t$ , but between  $40^{\circ}$  and  $50^{\circ}$  the curve changes in direction, and from  $50^{\circ}$  to  $150^{\circ}$  the equation is  $S = 52.3 + 0.0125t$ . The hydrate  $\text{NaBr} \cdot 2\text{H}_2\text{O}$  loses its water of crystallisation at  $50^{\circ}$ . When the ratio between anhydrous salt and water in a saturated solution is represented in molecules, numbers are obtained in the case of the majority of very soluble salts closely approaching those given by solid hydrated salts, and it would seem as if salts of the first class behaved like fused hydrates. For sodium bromide at  $-20^{\circ}$ , the ratio is  $\text{NaBr} : 8\text{H}_2\text{O}$ ; at  $+40^{\circ}$   $\text{NaBr} : 5.5 \text{H}_2\text{O}$ ; whilst from  $50$ — $150^{\circ}$  the ratio only varies from  $\text{NaBr} : 4.5 \text{H}_2\text{O}$  to  $\text{NaBr} : 4.3 \text{H}_2\text{O}$ , or approximately  $2\text{NaBr} + 9\text{H}_2\text{O}$  through an interval of  $100^{\circ}$ .

*Sodium Iodide*.—From  $0^{\circ}$  to  $80^{\circ}$   $S = 61.3 + 0.1712t$ , with extreme ratios  $\text{NaI} : 5\text{H}_2\text{O}$ , and  $\text{NaI} : 3\text{H}_2\text{O}$ . From  $80$ — $160^{\circ}$ ,  $S = 75 + 0.02586t$ ; with ratios  $\text{NaI} : 3\text{H}_2\text{O}$  and  $\text{NaI} : 2\text{H}_2\text{O}$ . Below zero the solubility appears to diminish very rapidly. According to Coppet (*Ann. Chim. Phys.*, 1884) the solubilities of the hydrates  $\text{NaBr} \cdot 2\text{H}_2\text{O}$  and  $\text{NaI} \cdot 2\text{H}_2\text{O}$  should be represented by curved lines, but the author's results show that the inflection of the curve near the point at which the hydrates are dissociated can be regarded as an inclination of the whole curve towards the axis  $x$  only when the curve is not sufficiently prolonged.

*Potassium Chloride*.—The solution freezes at about  $-9^{\circ}$ . Between  $-9^{\circ}$  and  $110^{\circ}$ ,  $S = 20.5 + 0.1445t$ , with  $\text{KCl} : 15\text{H}_2\text{O}$  and  $\text{KCl} : 6\text{H}_2\text{O}$ .

*Potassium Bromide*.—According to Kremers, the curve consists of two straight lines, but according to Coppet (*loc. cit.*), the solubility is represented by a single straight line. The author's results agree with those of Kremers between  $-12^{\circ}$  and  $+165^{\circ}$ , and Coppet's numbers are represented by this curve with greater accuracy than by the curve which he himself gives. The ratios are, at  $-12^{\circ}$   $\text{KBr} : 13\text{H}_2\text{O}$ ; at  $30^{\circ}$ ,  $\text{KBr} : 11\text{H}_2\text{O}$ ; at  $120^{\circ}$ ,  $\text{KBr} : 5\text{H}_2\text{O}$ .

*Potassium Iodide*.—The author's results agree with those of Coppet between  $0^{\circ}$  and  $100^{\circ}$ , but according to the latter the curve is a straight line below  $0^{\circ}$ , whilst the author finds that it is inflected, as in the case of the bromide. Between  $0^{\circ}$  and  $165^{\circ}$  the equation is  $S = 55.8 + 0.122t$ , with ratios at  $0^{\circ}$ ,  $\text{KI} : 7\text{H}_2\text{O}$ ; at  $120^{\circ}$ ,  $\text{KI} : 3.7\text{H}_2\text{O}$ .

The curves of the six haloïd salts already described are almost parallel. The curves of potassium bromide and iodide show pertur-

bations strictly comparable with those observed in the case of the hydrated salts, although no definite hydrates of these salts have been prepared.

**Calcium Chloride.**—Between  $-18^{\circ}$  and  $+6^{\circ}$  the proportion of anhydrous salt in a solution of the hydrate is given by the equation  $S = 32 + 0.2148t$ ; with extreme ratios,  $\text{CaCl}_2 : 13\text{H}_2\text{O}$  and  $\text{CaCl}_2 : 10\text{H}_2\text{O}$ . Between  $6^{\circ}$  and  $48^{\circ}$  the curve is modified, whilst from  $50^{\circ}$  to  $170^{\circ}$ , an interval of  $120^{\circ}$ , the equation is  $S = 54.5 + 0.0755t$ . The alterations in the curve do not take place suddenly at a point, as in the case of sodium sulphate. Up to  $+6^{\circ}$ , and even up to  $40^{\circ}$ , the crystallisation of saturated solutions takes place readily, but above  $40^{\circ}$ —the melting point of the hydrate—crystallisation takes place with difficulty, and the solution remains supersaturated for a long time.

When a cold saturated solution of calcium or magnesium chloride is mixed with cobalt chloride solution, the latter becomes blue, and a solution of nickel chloride becomes yellow, thus showing that all the water in these solutions is utilised in some way, and that the solution even exerts a dehydrating action. A saturated solution of zinc chloride has not this property. Saturated solutions in fact undergo double decomposition, independently of any definite hydrates which they may contain. Barium and strontium chlorides are completely precipitated from their solutions by a saturated solution of hydrated calcium chloride,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ .  
C. H. B.

**Permeability of Silver to Oxygen.** By L. TROOST (*Compt. rend.*, 98, 1427—1429).—A silver tube of 10 mm. internal diameter, with walls 1 mm. thick, was heated in cadmium vapour in an iron muffle, provided with an internal platinum lining. A slow current of oxygen was passed into the muffle, and the silver tube was rendered vacuous. Under these conditions oxygen passes through the walls of the tube with a velocity corresponding with 1.7 litre per square metre per hour. If the walls of the tube are only 0.5 mm. thick, the velocity of transfusion increases to 3.33 litres per hour. When a current of air is led into the muffle instead of oxygen, oxygen passes into the silver tube free from any trace of nitrogen, but the velocity of transfusion is only 0.89 litre per hour if the walls of the tube are 1.0 mm. thick.

Instead of maintaining a vacuum in the silver tube, a current of carbonic anhydride or some other gas may be led into it, but in this case the rate of transfusion is considerably lower. With a silver tube with walls 0.5 mm. in thickness, the rate of transfusion at the boiling point of cadmium is 0.4 c.c. per hour per square metre for carbonic anhydride; 0.1 c.c. for carbonic oxide; and less than 0.1 c.c. for nitrogen. This difference between the rates of transfusion of oxygen and nitrogen may possibly be utilised as a means of obtaining oxygen from the air.

The transfusion of oxygen through silver can be distinctly recognised at the boiling point of selenium.  
C. H. B.

**Soldering of Aluminium.** By BOURBOUZE (*Compt. rend.*, 98, 1490).—Aluminium can be readily soldered by means of an alloy of

tin and zinc, or better, of tin, bismuth, and aluminium. The best results are obtained with alloys of tin and aluminium. A good solder for articles which have to be beaten, turned, &c., is composed of 45 parts of tin and 10 parts of aluminium. Softer solders are obtained by using a smaller proportion of aluminium. The surface of aluminium requires no special preparation, but it is advisable to give surfaces of other metals a preliminary coating of pure tin. C. H. B.

**Melting Points of Beryllium Chloride and Bromide.** By T. CARNELLEY (*Ber.*, 17, 1357—1360).—In a paper on the vapour-density of beryllium chloride by Nilson and Pettersson (this vol. p. 820), some doubt is thrown on the accuracy of the author's determination of the melting point of beryllium chloride, inasmuch as the vapour-density of the chloride could be determined at the ordinary pressure at temperatures 100—150° lower. The author has therefore felt it necessary to publish the details of his determinations in order to show their correctness. He points out that many substances are known to sublime at temperatures considerably below their melting points.

A. J. G.

**Purification of Arseniferous Zinc.** By L. L'HÔTE (*Compt. rend.*, 98, 1491—1492).—Zinc containing arsenic or antimony can be easily purified by projecting into the fused metal 1 to 1.5 per cent. of anhydrous magnesium chloride, and agitating so long as white fumes are given off. Arsenic and antimony are volatilised as chlorides, and the metal is granulated in the usual way. C. H. B.

**Action of Copper Chlorides on Metallic Sulphides.** By F. RASCHIG (*Ber.*, 17, 697—698).—The results given below were obtained by boiling the freshly-precipitated metallic sulphides with solutions of cuprous or cupric chloride. The following sulphides, FeS, CoS, ZnS, CdS, PbS, Bi<sub>2</sub>S<sub>3</sub>, SnS, and SnS<sub>2</sub>, when boiled with a solution of cuprous chloride in sodium chloride, yield cuprous sulphide and the chlorides of the respective metals, or the products of their decomposition by water. When boiled with a dilute solution of cupric chloride, they yield cupric sulphide and the metallic chloride, except in the case of SnS, when cuprous sulphide, cuprous chloride, and a stannic compound are obtained, some sulphur being separated and some oxidised to sulphuric acid. Mercuric sulphide gives with cuprous chloride a yellow addition product of the formula HgS.CuCl; with dilute solutions of cupric chloride, it yields the same product, in addition to the compound, 2HgS.HgCl<sub>2</sub>, already known.

A. J. G.

**Cupric Iodide.** By M. TRAUBE (*Ber.*, 17, 1064—1067).—On adding a very dilute solution of potassium iodide to a dilute solution of cupric sulphate, the separation of iodine, with precipitation of cuprous iodide, takes place very slowly. A solution of  $\frac{1}{3}$  per cent. potassium iodide, when added to a 1 per cent. solution of cupric sulphate, only produces a precipitate in 10 minutes; one of  $\frac{1}{4}$  per cent. becomes yellow in one hour; and one containing  $\frac{1}{20}$  per cent. remains clear and colourless, does not give a blue coloration with starch solution, but gives the reaction of a cupric salt with caustic potash.



and potassium ferrocyanide. The author also finds that on sufficiently diluting a liquid containing a suspended precipitate of cuprous iodide and free iodine, in time the whole of the cuprous iodide is dissolved and the clear solution gives no reaction with starch solution; and that an aqueous solution of iodine may be freed from iodine by shaking it with an excess of cuprous iodide, owing to the formation of cupric iodide. This solution of cupric iodide is decomposed by ferrous sulphate in presence of hydrogen peroxide in acid solution, and in this it may be distinguished from other metallic iodides.

A. B.

**Action of Cupric Sulphide on Potassium Sulphide.** By A. DITTE (*Compt. rend.*, 98, 1429—1432).—When freshly precipitated cupric sulphide is mixed with a cold concentrated solution of potassium monosulphide, the liquid becomes orange-yellow, and after some hours the precipitate is converted into a mass of crystals, partly quadratic or octagonal plates, deep red by transmitted light, partly long slender needles with brilliant greenish facets. If the liquid is boiled, the cupric sulphide changes almost instantly into a bulky mass of slender needles, with a bronze colour and metallic lustre. All these crystals have the composition  $K_2S_4Cu_2S$ . If the alkaline sulphide solution is below a certain degree of concentration, the cupric sulphide is not altered even after several months.

This reaction is similar to that already observed in the case of mercuric sulphide, but the cupric sulphide is at first decomposed into cuprous sulphide and sulphur. The reaction  $6CuS$ , solid +  $K_2S$ , dissolved =  $3Cu_2S$  solid +  $K_2S_4$  dissolved, develops approximately + 4.6 cal., but the concentration of the solution may change the sign of the thermal disturbance, and hence below a certain degree of concentration the cupric sulphide is not attacked. That the cupric sulphide is first decomposed in this manner is shown by the fact that when it is brought in contact with the colourless solution of potassium monosulphide, the latter becomes orange-yellow and behaves with acids like solutions of polysulphides. The precipitated cupric sulphide is not a mixture of cuprous sulphide and sulphur as Thomsen has supposed, for when brought in contact with an alkaline sulphide solution too dilute to convert it into the compound  $K_2S_4Cu_2S$ , the alkaline sulphide does not take up sulphur, although a solution of the same strength readily dissolves free sulphur.

The double sulphide can also be obtained in long needles by immersing metallic copper in a solution of the alkaline sulphide. If the liquid is exposed to air, the amount of the double compound gradually increases, but if it is contained in a closed vessel, the formation of the double sulphide ceases after a time. The action of the alkaline sulphide on the copper is due to the presence of oxygen, for if the solution is perfectly free from oxygen and the latter is carefully excluded, the copper is not attacked. The first reaction consists in the formation of potassium hydroxide and cupric sulphide, and the latter as fast as it is formed splits up into cuprous sulphide, which forms the double compound  $K_2S_4Cu_2S$ , and sulphur, which forms polysulphides. The reaction  $K_2S$  diss. +  $O + Cu = K_2O$  diss. +  $CuS$

solid, develops + 62.4 cal., and continues until all the oxygen is used up. The polysulphide which is formed, in its turn acts on the copper with formation of the double sulphide and potassium monosulphide, and at the end of the reaction the solution is quite colourless.

A solution of potassium sulphide too dilute to decompose cupric sulphide attacks metallic copper in presence of air or oxygen, but the product is the simple sulphide  $\text{CuS}$ .  
C. H. B.

**Action of Mercuric Sulphide on Potassium Sulphide.** By A. DITTE (*Compt. rend.*, **98**, 1380—1382).—The compound  $\text{K}_2\text{S}_5\text{HgS}$  can be obtained in red needles similar in every respect, except colour, to the black crystals previously described (this vol., p. 893). These red crystals are formed when a solution of the alkaline sulphide containing an excess of mercuric sulphide is gradually heated to  $35\text{--}40^\circ$ , especially if a small quantity of vermilion is added. In such a solution, heated at  $35\text{--}40^\circ$ , but still clear, the formation of red or black needles is determined by adding a small quantity of vermilion or of the black crystals. The colour of the crystals varies from bright red to deep cinnabar-red, according to the concentration of the solution and the temperature. When a mass of the black needles is allowed to stand in the alkaline sulphide solution in a closed vessel for some time, those crystals which are in contact with the sides of the vessel are gradually converted into the red variety. These are stable in the alkaline liquid in the cold, but if heated they are reconverted into the black variety, the change being more rapid the more concentrated the solution.

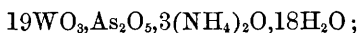
If the alkaline sulphide solution at the ordinary temperature contains but a small quantity of the compound  $\text{HgS}, \text{K}_2\text{S}$ , it yields on boiling a black deposit, which contains not only black crystals of  $\text{K}_2\text{S}_5\text{HgS}$ , but also mercuric sulphide in black hexagonal plates. If such a solution is gradually heated in a water-bath and mixed with a trace of vermilion, a red deposit is obtained consisting of red needles of the composition  $\text{K}_2\text{S}_5\text{HgS}$ , and red transparent rhomboidal lamellæ of mercuric sulphide. With a certain degree of concentration of the solution, the latter is practically the sole product.

It is evident, therefore, that the simple sulphide  $\text{HgS}$  and the double sulphide  $\text{K}_2\text{S}_5\text{HgS}$  can be obtained simultaneously in either red or black crystals, but when one is red the other is red, and when one is black the other is also black.

These facts explain the wet process for the manufacture of vermilion. In this process precipitated black mercuric sulphide is digested with potassium sulphide solution, care being taken that the temperature does not rise above  $45^\circ$ . A certain quantity of the double sulphide  $\text{K}_2\text{S}_5\text{HgS}$  is formed, but as the temperature of the liquid, which is not constant, rises slightly, the double compound is decomposed and yields red crystalline mercuric sulphide. When the temperature falls somewhat, a further quantity of the double compound is formed at the expense of the more easily attacked amorphous sulphide. This in its turn is decomposed by the next rise of temperature, and so on until the whole mass is converted into vermilion.

C. H. B.

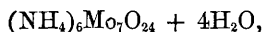
**Arsenotungstic Acids.** By M. FREMERY (*Ber.*, 17, 296—297).—By decomposing barium tungstate,  $\text{BaWO}_4$ , suspended in an aqueous solution of arsenic acid, with the calculated quantity of sulphuric acid and digesting on the water-bath, the author obtained a golden-yellow solution, which, when concentrated in a vacuum over sulphuric acid, yielded crystals of an *arsenotungstic acid* in the form of long hexagonal plates. These crystals are stable, and the saturated solution at  $16^\circ$  has a sp. gr. of 3.279. Carbonates, when added to the aqueous solution of this acid, cause it to split up again into its constituents, but crystallisable salts were obtained by adding the nitrates of the metals and concentrating on the water-bath. The *potassium, sodium, ammonium, copper, cobalt, and nickel salts* crystallise well; the *barium salt* is microcrystalline, and the *silver salt* forms a brown precipitate. The analytical results obtained for the ammonium salt correspond approximately with the constitution



and for the potassium salt with  $19\text{WO}_3, \text{As}_2\text{O}_5, 3\text{K}_2\text{O}, 16\text{H}_2\text{O}$ .

The author also obtained a second arsenotungstic acid differing from the first in crystalline form, and in the density of its saturated solution, which is 2.241 at  $16^\circ$ . L. T. T.

**Action of Hydrogen Peroxide on Molybdates.** By C. BAERWALD (*Ber.*, 17, 1206).—Commercial ammonium molybdate,



dissolves in hydrogen peroxide, forming a yellow solution, which deposits lemon-coloured crystals belonging to the monoclinic system—

$$a : b : c = 1.4727 : 1 : 1.0268. \quad \beta = 74^\circ 32'.$$

Similar compounds of potassium, sodium, magnesium, barium, silver, and lead were prepared. W. C. W.

**Reduction of Molybdenum Sulphide.** By O. F. V. D. PFORDTEN (*Ber.*, 17, 731—736).—Both the bisulphide and trisulphide of molybdenum are completely reduced to metal when strongly heated in a current of dry hydrogen. In the case of the native sulphide (molybdenum glance), whose reduction is slightly more difficult to effect than that of the artificial sulphides, the metal is obtained in pseudomorphs of the mineral. It appears to be more convenient to prepare the metal in this way from the sulphide than by reduction of the oxide, the method usually employed. In estimating molybdenum, it is better to weigh as metal than as bisulphide, as there is some fear of the latter being partially reduced during the heating in hydrogen.

A. J. G.

**Ferrous Chloride.** By V. MEYER (*Ber.*, 17, 1335—1338).—The author has redetermined the vapour-density of this substance, using a porcelain vessel and an atmosphere of hydrochloric acid gas. The hydrochloric acid prevents the decomposition, which was previously noted, of a trace of the ferrous chloride into iron and ferric chloride. The numbers obtained were 6.67 and 6.38.  $\text{FeCl}_2$  re-

quires 4.39,  $\text{Fe}_2\text{Cl}_4$  8.78. It would seem, therefore, that ferrous chloride, like stannous chloride, has the double molecule  $\text{Fe}_2\text{Cl}_4$  at low temperatures, the simple one  $\text{FeCl}_2$  at high temperatures, but that the temperature employed (bright yellow heat) was not high enough to cause the complete formation of the simpler molecules. L. T. T.

**Colloidal Derivatives of Ferric Hydroxide.** By E. GRIMAUZ (*Compt. rend.*, **98**, 1485—1488 and 1540—1542).—When potassium hydroxide is added to a mixture of glycerol and ferric chloride, a precipitate is formed soluble in excess, and the solution has the characteristic properties of the colloidal solutions previously described (this vol., p. 905). The tendency to coagulate is diminished by the presence of a large amount of glycerol, and increased by the presence of sodium chloride or of potash in excess. If the proportion of glycerol is very large, coagulation is entirely prevented. When solutions rich in glycerol are dialysed, they first lose their excess of potash, then their excess of glycerol, and become coagulable by heat, and finally they form a firm thick jelly containing glycerol, ferric hydroxide, and potash. Similar solutions are obtained by substituting either ammonia or soda, or sodium or potassium carbonate for potash. They seem to be compounds of glycerol, ferric hydroxide, and alkalis, and are easily dissociated by water into glycerol and insoluble compounds richer in ferric hydroxide. With acetic acid, they yield a precipitate soluble in excess, and this solution gives a greenish precipitate with potassium ferrocyanide, converted into Prussian blue by the action of a mineral acid.

Mannitol, erythrol, and sugar yield solutions having precisely similar properties.

Ferropotassium tartrate also forms colloidal solutions with similar properties, but they are not precipitated by potash in the cold, and the precipitate with carbonic anhydride is ochreous, and resembles ferric hydroxide. Potassium ferrocyanide produces a violet coloration, and Prussian blue is precipitated from this solution on adding an acid.

When a solution of ferric chloride is added to a solution of sodium arsenate, a precipitate of ferric arsenate is formed, but redissolves in excess of ferric chloride, forming a colloidal solution, which yields an opaque yellowish-white coagulum of the composition  $\text{Fe}_2(\text{AsO}_4)_2$ . In preparing this solution, excess of ferric chloride must be avoided, since this substance prevents coagulation by heat. If the solution is dialysed, it loses sodium chloride, and the jelly which forms is perfectly transparent and of a pale yellow colour, but by prolonged dialysis it becomes reddish-yellow.

Potassium arsenite and ferric chloride yield a similar solution, which is very unstable, and coagulates spontaneously. With potash, it forms a precipitate soluble in excess, and when this solution is dialysed it yields a colloidal solution of ferropotassium arsenite, which does not gelatinise on heating unless mixed with potash solution, when a thick brown jelly resembling ferropotassium tartrate is formed. Arsenious acid therefore resembles tartaric acid in its behaviour with ferric salts.

Boric acid and sodium phosphate behave like arsenic acid, but in

the case of the phosphate the solution shows less tendency to coagulate.

A 2.26 per cent. solution of silica, obtained by the decomposition of methyl silicate, forms with ferric chloride and excess of potash a limpid solution, which becomes turbid after a few minutes.

C. H. B.

**Hydrates of Cobaltous Chloride.** By A. POTILITZIN (*Ber.*, 17, 276—283).—As is well known, hydrated cobaltous chloride changes in colour under varying conditions of temperature, &c. Bersch (*Sitzungsber. d. Wiener Akad.*, 56, 724) states that three hydrates exist, namely,  $\text{CoCl}_2 + 6\text{H}_2\text{O}$ , which is red in colour at ordinary temperatures, melts at  $86^\circ$ , and begins to lose water at  $111^\circ$ ; a rose-coloured  $\text{CoCl}_2 + 4\text{H}_2\text{O}$ , formed from the hexhydrate at  $116^\circ$ ; and  $\text{CoCl}_2 + 2\text{H}_2\text{O}$ , formed from the two last-named hydrates by heating them at  $121^\circ$ . He further states that all these hydrates when heated turn blue, the dihydrate existing in two modifications, even at ordinary temperatures; the one mentioned above being of a dark violet colour, the other, obtained by drying the hexhydrate over sulphuric acid, forming a rose-coloured crystalline powder having a slight violet tint, and finally that all lose water at  $140^\circ$  and yield the anhydrous salt.

The author has reinvestigated this subject, and cannot confirm Bersch's statements. Crystals of the hexhydrate begin to lose water at about  $30$ — $35^\circ$ , and at  $45^\circ$  effloresce tolerably quickly, about four hours' heating at the latter temperature converting them into the dihydrate, which is of a rose colour, having a slight tint of violet. This same dihydrate is obtained if the hexhydrate is kept four or five days over sulphuric acid under a bell-jar. The colour, &c., is identical in both cases. The dihydrate absorbs moisture when exposed to the air, and becomes reconverted into the hexhydrate. At a little below  $100^\circ$ , the dihydrate is very slowly converted into a dark violet monohydrate, which is exceedingly hygroscopic, absorbing moisture from the air, and being reconverted into the hexhydrate. When a solution of  $\text{CoCl}_2 + 6\text{H}_2\text{O}$  in absolute alcohol is slowly evaporated in an air-bath at  $90$ — $95^\circ$ , it deposits the same monohydrate in the form of fine silky violet-coloured needles. In very thin layers, this salt is almost colourless, and as the thickness of the layers increases the colour passes through various shades of violet, until with a thick layer it is almost the same as that of a concentrated alcoholic solution of cobaltous chloride. At  $110$ — $120^\circ$  the monohydrate loses its last molecule of water, but this is always accompanied by a slight loss of hydrochloric acid, the anhydrous salt thus formed always leaving a slight brown residue of oxide when dissolved. The anhydrous salt rapidly absorbs moisture if exposed to the air.

The author draws the following conclusions from the results obtained:—The temperatures given by Bersch for the decomposition and formation of the various hydrates are arbitrary and incorrect. The dihydrate  $\text{CoCl}_2 + 2\text{H}_2\text{O}$  exists only in one form, and is of a rose colour with a slight shade of violet. There are three distinct hydrates of cobaltous chloride,  $\text{CoCl}_2 + 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2 + 2\text{H}_2\text{O}$ , and  $\text{CoCl}_2 + \text{H}_2\text{O}$ . The change of colour which occurs on heating is due to the separation of the water; all dehydrating agents (as alcohol,

hydrochloric acid, &c.) may therefore cause change of colour even at low temperatures.

The author suggests that the incorrectness of Bersch's results is probably due to his not allowing time for the dissociation to be completed. Even porous hygroscopic substances, such as filter-paper, cause dehydration of these salts; a drop of a concentrated aqueous solution of cobaltous chloride placed on filter-paper always shows a blue edge as it dries.

L. T. T.

### Compounds of Gold Chlorides with Phosphorus Chlorides.

By L. LINDET (*Compt. rend.*, 98, 1382—1384).—*Aurous phosphorous chloride*,  $\text{Au}_2\text{Cl}_3 \cdot 2\text{PCl}_3$ , is obtained by heating aurous chloride (prepared by reducing auric chloride at  $185$ — $190^\circ$ ) with excess of phosphorous chloride in sealed tubes at  $110$ — $120^\circ$  for an hour. The aurous chloride dissolves in the phosphorous chloride, and on cooling the double chloride is deposited in large colourless oblique prisms. The double chloride is stable in dry air, and is infusible and non-volatile, but it decomposes above  $100^\circ$  with evolution of phosphorous chloride, and a complex residue is left. When treated with water or exposed to moist air, it is decomposed with formation of phosphorous acid and metallic gold. Chlorine and phosphoric chloride convert it into the double auric phosphoric chloride.

*Auric phosphoric chloride*,  $\text{AuCl}_3 \cdot \text{PCl}_3$ , can be obtained by the direct combination of auric chloride and phosphoric chloride, but it is most easily prepared by heating aurous chloride in sealed tubes at  $120$ — $130^\circ$  for several hours with a solution of two equivalents of phosphoric chloride dissolved in phosphorous chloride. It forms citron-yellow microscopic needles, which are insoluble in and are not attacked by phosphorous chloride, but in contact with metallic gold and phosphorous chloride, they are reduced to aurous phosphorous chloride. At about  $120^\circ$ , it dissociates into auric chloride and phosphoric chloride; it is decomposed by water.

Both these compounds can be produced simultaneously by treating auric chloride with phosphorous chloride at  $120^\circ$ , or by treating metallic gold with phosphoric chloride. In the latter case, one or the other double salt can be obtained alone by using proper proportions of gold and of phosphoric chloride.

C. H. B.

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### Mineralogical Chemistry.

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**Rubidium, Cæsium, Lithium, and Boric Acid in Chili Salt-petre.** By DIEULAFAIT (*Compt. rend.*, **98**, 1545—1548).—Grandeau found in 1863 that the beetroots in the north of France contain a relatively large proportion of rubidium, but are free from cæsium and lithium, but in beetroots from Lower Normandy, where no foreign substances had been used as manure, the author found neither

cæsium nor rubidium, but distinct traces of lithium. In the north of France, Chili saltpetre is largely used as a manure, and the author finds that sodium nitrate from Chili and Peru, even after being once refined, contains sensible quantities of rubidium, mere traces of lithium, little or no cæsium, and an unusual quantity of boric acid. The source of the rubidium in the beetroot is obvious.

C. H. B.

**Minerals from Upper Silesia.** By B. KOSMANN (*Jahrb. f. Min.*, 1884, 2, Ref., 15—17).—The author has already published a paper on the same subject (Abstr., 1883, 955). He now describes at some length the minerals occurring in the ore deposits of the Muschelkalk of Upper Silesia. The minerals described are—zinc blende, iron pyrites, cerussite, dialogite, tarnowitzite, and calcite. Analyses of markasite from the Apfel Mine (1) and from Bleischarley (2) are given :—

	Fe.	Ni.	Pb.	Zn.	As.	S.	SiO <sub>2</sub> .
I.	43·51	0·25	0·51	0·078	2·12	48·55	1·32
II.	42·27	0·185	0·124	0·147	0·71	50·15	1·30

	Al <sub>2</sub> O <sub>3</sub> .	CaO.	Total.
I.	0·89	2·78	100·008
II.	0·87	2·06	99·816

This the author believes to be a mixture of markasite, arsenical pyrites, nickel pyrites, blende, galena, and a silicate, CaAl<sub>2</sub>SiO<sub>6</sub>.

B. H. B.

**Thenardite.** By O. MÜGGE (*Jahrb. f. Min.*, 1884, 2, Mem., 1—10).—By observing the optical properties, at various temperatures, of natural and artificial thenardite (Na<sub>2</sub>SO<sub>4</sub>), as well as those of the mixed crystals of K<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>, the author arrives at the conclusion that the theory of morphotropic relations between glaserite (K<sub>2</sub>SO<sub>4</sub>) and thenardite is, to a certain extent, correct.

In order to obtain artificial thenardite, Glauber's salt was heated not much above 45°; the interior of the crystals then fused, and, on cooling, a cavity was formed, lined with small transparent crystals of thenardite. Glauber's salt crystals, dried below 35°, give up their water, and pass over into amorphous thenardite. The mixed salt of equal parts of potassium and sodium sulphates crystallises optically uniaxial, and is positively doubly refracting. When heated, however, it becomes first isotropic and then optically negative. Pure potassium sulphate presents two similar modifications; the rhombohedral crystals are positive, whilst glaserite, on being heated, passes over into a hexagonal modification with negative double refraction. The author has also no doubt that thenardite, on being heated to 180—250°, passes over into a hexagonal modification, the true nature of which is observed with greater difficulty than in the salts previously mentioned, on account of its very weak double refraction. Similar weak double refraction has been observed in the double salt of potassium and lithium sulphates, whilst the double salt of potassium and



sodium approaches an isotropic state only at a much higher temperature.

It is more difficult to explain how it is that the uniaxial modification of sodium sulphate, produced by heating the rhombic salt, is just as irregularly disposed as that obtained by fusion. The geometrical deviation from hexagonal symmetry is greater with thenardite than with glaserite. The slight variation of the refractive indices of the uniaxial modification, like their change in the mixed salt, perhaps indicates at the same time an approach to regular symmetry.

In conclusion, the author is of opinion that it is not merely by chance that the majority of the substances hitherto examined approach with increasing temperature a higher symmetry, or reach it, as in the case of arragonite, nitre, glaserite, silver iodide, leadhillite, and cryolite, but not of sulphur and mercury iodide; these substances pass over gradually, from the most highly differentiated crystalline state into the amorphous fluid state, so far as they can reach it without decomposition.

B. H. B.

**Triclinic Potash Soda Felspar (Microclase).** By F. J. WILK (*Jahrb. f. Min.*, 1884, 2, Ref., 20).—The author proposes to apply the name microclase to the triclinic felspars, which stand nearer to orthoclase than albite, but are distinguished from the former by the crystal system, and from microcline by the small extinction angle on the base, and from both by the percentage of soda. He describes a felspar of this class from St. Gotthard. The angle  $OP : \infty P \infty$  gave on an average  $90^\circ 24'$ . Sp. gr. 2.567. The analysis gave the following results (I):—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	K <sub>2</sub> O.	Na <sub>2</sub> O.	Total.
I.	(66.40)	16.23	11.90	5.47	100.00
II.	(66.20)	18.87	10.37	4.56	100.00

A combination of  $3K_2Al_2Si_6O_{16}$  with  $2Na_2Al_2Si_6O_{16}$ , would require the figures given under II.

B. H. B.

**Analysis of the Foyaite from the Serra de Monchique, Portugal.** By P. JANNASCH (*Jahrb. f. Min.*, 1884, 2, Mem., 11--13). --The analysis gave the following results:—

SiO	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.
54.20	1.04	21.74	0.46	2.36	0.11	1.95	0.52

K <sub>2</sub> O.	Na <sub>2</sub> O.	Li <sub>2</sub> O.	Loss on ignition.	Total.	Sp. gr.
6.97	8.69	trace	2.32	100.36	2.578

B. H. B.

**New Locality for Andesine at Orijärvi, in Finland.** By H. GYLLING (*Jahrb. f. Min.*, 1884, 2, Ref., 19).—On the crystals, the following planes were observed:— $0P$ ,  $\infty P \infty$ ,  $\infty P \infty$ ,  $\infty P'$ ,  $\infty' P$ ,  $\infty P' \infty$ ,  $\infty' P'$ ,  $2' P' \infty$ ,  $'P$ ,  $P'$ ,  $'P$ ,  $2P$ ,  $2P'$ .

The analysis gave:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	Na <sub>2</sub> O.	Loss.	Total.	Sp. gr.
57·37	26·09	8·13	7·96	0·70	100·25	2·68

B. H. B.

**Solubility of the Labradorite from St. Paul Island.** By P. JANNASCH (*Jahrb. f. Min.*, 2, Mem., 42—44).—These experiments were undertaken to solve the question whether the feldspars, regarded as an isomorphous mixture of sodium-aluminium and calcium-aluminium silicates, when treated with hydrochloric acid, give up the anorthite portion, or whether the whole of the feldspar substance is partially soluble. The results are in favour of the latter view. I is the analysis of the labradorite (sp. gr. 2·688); II, that of the acid solution; and III, that of the feldspar remaining insoluble in hydrochloric acid:—

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	Loss on ignition.	K <sub>2</sub> O.
I.	54·09	27·82	1·50	trace	11·20	0·05	0·19	0·43
II.	52·23	26·96	1·98	trace	13·25	0·12	—	0·23
III.	54·34	29·36	0·22	trace	10·79	—	—	0·46

	Na <sub>2</sub> O.	Li <sub>2</sub> O.	Total.
I.	4·76	trace	100·04
II.	5·23	trace	100·00
III.	5·49	—	100·66

B. H. B.

**Relation between the Optical Properties and Chemical Composition of Pyroxene and Amphibole.** By F. J. WINK (*Jahrb. f. Min.*, 1884, 2, Ref., 21).—The following data serve as an addition to the former paper on the same subject (Abstr., 1883, 560):—

	FeO per cent.	Extinction angle on clinopinacoid.
Diopside from Achmatowsk .....	2·00	37° 30'
Diopside from Pargas .....	2·25	38
Diopside from Ala .....	—	39
Diopside from Zillerthal .....	2·51	38°—39°
Augite from Nordmarken ....	17·31	45° 45'
Augite in the olivine diabase of Ewra (West Finland) .....	18·35	46°

The examination of a number of augites from basaltic rocks gave results which do not agree with the series.

	FeO per cent.	Extinction angle on clinopinacoid.
Augite from basalt tuff from Teplitz .	5·45	46° 30'
Augite from Monti Rossi .....	7·89—11·39	48° 50'
Augite from Vesuvius .....	4·55—9·08	45° 30' and 49°
Augite from Frascati .....	10·80	54°

The author is therefore of opinion that a basaltic augite must be distinguished analogous to the basaltic hornblende. The latter also seems to have optical properties different from the ordinary hornblende occurring in older rocks. The hornblende from the basalt-wake of Schima, with an alumina percentage of 17.59, gave an extinction angle on the clinopinacoid of only  $10^\circ$ . B. H. B.

**Kelyphite.** By A. SCHRAUF (*Jahrb. f. Min.*, 1884, 2, Mem., 21—26).—If the large amphibole group be divided into two classes of nearly equal form and optical symmetry, namely, the actinolite division,  $\text{R}_2\text{SiO}_3$ , and the hornblende division,  $x(\text{R}_2\text{SiO}_3) + y(\text{R}_2\text{SiO}_4)$ , in which  $y$  is greater than  $x$ , kelyphite may be identified with hornblende. B. H. B.

**Ganomalite.** By A. SJÖGREN (*Jahrb. f. Min.*, 1884, 2, Ref., 23—24).—This mineral, discovered by Nordenskiöld at Laangban (Abstr., 1879, 22), has recently been obtained from Jakobsberg, in Nordmarken. System tetragonal. Columnar crystals with the planes:  $\infty\text{P}$ ,  $\text{P}$ ,  $\infty\text{P}_4$ ,  $0\text{P}$ .  $\infty\text{P} : \text{P} = 135^\circ$ . Cleavage distinct, parallel to  $\infty\text{P}$  and  $0\text{P}$ . Fracture uneven.  $\text{H.} = 3$ . Sp. gr. 5.738. Colourless, greasy to glassy lustre. Becomes dull and whitish on exposure by the oxidation of the lead. Optically positive. Strong refraction. Weak interference colours. Fuses in thin splinters in candle flame. Soluble in warm nitric acid. The analyses, made with impure material, lead to the formula  $2\text{PbO}, \text{CaO}, 2\text{SiO}_2$ . B. H. B.

**Analysis of Ganomalite.** By G. LINDSTRÖM (*Jahrb. f. Min.*, 1884, 2, Ref., 25).—Ganomalite, from Jakobsberg, carefully purified by the magnet and by iodide solution, gave on analysis the following results:—

$\text{SiO}_2$ .	$\text{PbO}$ .	$\text{CuO}$ .	$\text{MnO}$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{MgO}$ .
18.33	68.80	0.02	2.29	0.07	0.12	9.34	0.11
Alkalis.		$\text{P}_2\text{O}_5$ .	$\text{Cl}$ .	Ignition.		Total.	
0.10		0.04	0.24	0.57		100.03	

From this the formula  $3\text{PbO}, 2\text{SiO}_2 + 2\text{RO}, \text{SiO}_2$  is deduced.

B. H. B.

**Tephroite.** By A. SJÖGREN (*Jahrb. f. Min.*, 1884, 2, Ref., 24—25).—Crystals of tephroite from Laangban were found to belong to the rhombic system. Colour, grey; transparent; glassy to greasy lustre. Fracture conchoidal to splintery.  $\text{H.} = 5.5$  to 6. Sp. gr. 3.95—4.02. Fuses before the blowpipe with difficulty to a brownish cloudy glass. Gelatinises with warm hydrochloric acid. The following forms were observed:— $\infty\text{P}$ ,  $\infty\text{P}$ ,  $\infty\text{P}_2$ ,  $\infty\text{P}_3$ ,  $\text{P}$ ,  $2\text{P}_2$ ,  $3\text{P}_3$ . The analysis gave:—

$\text{SiO}_2$ .	$\text{MnO}$ .	$\text{MgO}$ .	Total.
31.39	65.34	3.15	99.88

B. H. B.

**The Rocks of Noyang.** By A. W. HOWITT (*Jahrb. f. Min.*, 1884, 2, Ref., 59—61).—The author describes the eruptive rocks occurring

at Omeo, Gippsland, Victoria. The rocks in the district are quartz-mica diorites (Analysis I), traversed by porphyritic masses. In contact with these dykes, porphyritic varieties of quartz-mica diorites (Analyses II and III) occur. Somewhat more recent than the quartz-mica porphyrites are dykes of quartz-porphyrite (Analysis IV), and quartz-felsophyrtes. The diorites and porphyrites are traversed by dykes of "greenstone." A greenstone dyke (Analysis V), about 30 inches wide, is described by the author as a diorite, not far removed from the amphibolised diabases. A true diabase dyke, the only one observed by the author, occurs in the quartz-mica diorite at Navigation Creek.

	I.	II.	III.	IV.	V.
SiO <sub>2</sub> .....	57·69	72·39	77·66	(78·77)	47·63
Al <sub>2</sub> O <sub>3</sub> .....	15·65	14·42	12·30	12·44	17·20
Fe <sub>2</sub> O <sub>3</sub> .....	7·42	0·56	0·61	0·95	3·60
FeO .....	2·41	0·30	0·17	—	8·09
MnO .....	trace	0·01	—	—	trace
CaO .....	6·92	0·85	0·16	0·53	6·42
MgO .....	3·10	1·85	0·73	0·02	6·25
K <sub>2</sub> O .....	2·37	1·23	0·19	0·24	1·31
Na <sub>2</sub> O .....	2·33	5·93	6·96	6·79	4·65
H <sub>2</sub> O .....	1·59	1·13	0·46	0·26	2·71
TiO <sub>2</sub> .....	0·03	—	—	—	1·39
P <sub>2</sub> O <sub>5</sub> .....	0·22	trace	—	—	trace
CO <sub>2</sub> .....	—	—	—	—	0·44
Total .....	99·73	98·67	99·24	100·00	99·69
Hygroscopic water....	0·34	0·55	0·33	0·14	0·73
Sp. gr.....	2·78	2·63	2·63	2·61	2·89

B. H. B.

**Rock from the Volcano Yate.** By H. ZIEGENSPECK (*Jahrb. f. Min.*, 1884, 2, Ref., 58).—Four specimens were examined from the Volcano Yate, south of the Boca de Reloncavi, South Chili. The first, from the northern foot of the volcano, is a porphyritic rock (Analysis II) containing felspar (Analysis I), olivine, augite, and magnetite. The ground-mass consists principally of felspar with augite crystals, and but little granular isotropic basis. The second sample, of a slag-like structure, contains felspar, augite, and magnetite in a brown isotropic basis. The third rock (Analysis III) contains plagioclase, augite, magnetite, and apatite in a dark ground-mass, poor in glass. The fourth rock (Analysis IV) is compact, and weathered on the surface. It contains plagioclase, augite, magnetite, and apatite in a microlithic ground-mass.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	K <sub>2</sub> O.
I.	46·03	32·41	1·78	—	—	13·78	0·28	0·75
II.	52·02	17·14	7·96	3·52	0·85	11·57	3·13	0·60
III.	63·69	15·03	2·51	2·41	0·55	3·30	0·80	2·46
IV.	63·49	12·42	6·41	1·34	0·85	4·17	1·32	1·78

	Na <sub>2</sub> O.	Loss on ignition.	Total.	Sp. gr.
I.	4.43	0.48	99.94	2.74
II.	2.38	0.28	99.45	2.76
III.	6.54	2.23	99.52	2.55
IV.	4.90	2.88	99.56	2.52

In Analyses II, III, and IV, traces of HCl, P<sub>2</sub>O<sub>5</sub>, and SO<sub>3</sub> were detected, and in III and IV also traces of copper. The author classes the first rock as basalt, the others as augite-andesite. B. H. B.

**Krakatoa Ashes.** By A. v. LASAULX, A. SAUER, J. H. KLOOS, A. RENARD, and A. DAUBRÉE (*Jahrb. f. Min.*, 1884, 2, Ref., 53—58).—There can be no doubt that the Krakatoa eruption yielded ashes of enstatite-andesite. All the observers give labradorite, augite, magnetite, and apatite. Hornblende and iron pyrites are also stated to be present by one observer. The principal mass of the ashes consists of a pumiceous glass.

The chemical composition of the ashes which fell in Batavia is determined by an analysis (I) by Sauer, and also by Renard (II). Sauer also found 0.82 substance soluble in water, consisting principally of lime and sulphuric acid, with traces of potash and soda. He also analysed the ashes carefully freed from crystalline substances, and found the composition given under III. Both Renard and Sauer also analysed a sample of ashes, collected from His Majesty's ship "Elizabeth," 300 nautical miles from the Sunda Straits. This was found to be identical with the material from Batavia.

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.
I.	63.30	1.08	14.52	5.82		4.00	1.66
II.	65.04	—	14.63	4.47	2.82	3.34	1.20
III.	66.73	0.50	16.59	4.08		3.82	1.50

	MnO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Loss on ignition.	Total.
I.	0.23	5.14	1.43	2.17	99.35
II.	trace	4.23	0.97	2.74	99.44
III.	trace	(5.65)		2.13	100.00

B. H. B.

**Krakatoa Ashes.** By K. OEBBEKE (*Jahrb. f. Min.*, 1884, 2, Mem., 32—33).—The author gives analyses of the ashes which fell on the ship "Barbarossa," on the 27th August, 1883. The results obtained by him were as follows:—I, complete analysis; sp. gr. 2.38. II, portion soluble in hydrochloric acid, 7 per cent. III, portion insoluble in hydrochloric acid, 93 per cent.

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.
I.	68·06	0·38	15·03	0·28	3·66	trace	2·71	0·81
II.	50·45	trace	14·05	17·10		—	5·65	3·80
III.	69·25	0·41	15·10	3·03		trace	2·50	0·59

	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	3·41	4·25	2·12	100·71
II.	1·95	2·65	5·10	100·75
III.	3·51	4·36	1·89	100·64

The original ashes contained substances soluble in water :—

CaO.	MgO.	Na <sub>2</sub> O.	Cl.	SO <sub>3</sub> .	K <sub>2</sub> O.	Total.
0·20	0·11	0·79	0·76	0·69	trace	2·55

or

NaCl.	NaSO <sub>4</sub> .	CaSO <sub>4</sub> .	MgSO <sub>4</sub> .	Total.
1·25	0·29	0·48	0·33	2·35

B. H. B.

**Analysis of Volcanic Ashes from Krakatoa.** By D. DE LOOS (*Ber.*, 17. 999—1000).—These ashes were collected after the eruption of August, 1883, in Java, and were found to consist of 0·80 per cent. of matter soluble in water (silica, sulphuric acid, chlorine, calcium, potassium, sodium), 5·70 per cent. soluble in acid (chiefly ferric oxide and alumina), and 93·50 per cent. of insoluble matter. This insoluble part consisted of 64·05 per cent. silica, 6·54 per cent. ferric oxide, and a trace of ferrous oxide, 13·08 per cent. alumina, and 1·80 per cent. calcium oxide.

A. B.

**Classification of Meteorites.** By G. TSCHERMAK (*Jahrb. f. Min.*, 1884, 2, Ref., 25—28).—The author proposes the following classification :—

I. Meteorites, consisting principally of iron.

Meteoritic iron.

II. Iron ground-mass, with enclosed silicates.

Pallasite—iron and olivine,

Mesosiderite—iron, olivine, and bronzite,

Siderophyr—iron and bronzite,

Grahamite—iron, plagioclase, olivine, bronzite.

III. Olivine and bronzite, with subordinate iron.

Chondrite.

IV. Olivine, bronzite, pyroxene.

Chassignite—olivine,

Amphoterite—olivine and bronzite,

Diogenite—bronzite or hypersthene,

Bustite—diopside and enstatite.

V. Augite, bronzite, and lime-felspar.

Howardite—augite, bronzite and plagioclase.

Eukrite—augite and anorthite.

B. H. B.

**Peculiar Concretions in Iron Meteorites.** By L. SMITH (*Amer. J. Sci.*, **25**, 417—423).—The author calls attention to the more or less globular concretions in the interior of meteoric iron, which seem but rarely to be absent. These concretions consist of troilite, schreibersite, graphite, daubréelite, lawrencite, or chromite. Each of these concretions is almost as characteristic of meteoric iron as the nickeliferous alloy of the metal. The troilite concretions are often somewhat complex in their character. 8 grams from the Cranbourne iron were treated with petroleum ether, dilute hydrochloric acid, and nitric acid, and the magnet was applied to the residue. In this way, celestialite, sulphur, a compound of sulphur and carbon, schreibersite, daubréelite, graphite, silica, and a cobalt mineral were determined.

B. H. B.

**The Bishopville and Waterville Meteorites.** By M. E. WADSWORTH (*Amer. J. Sci.*, **26**, 22—38).—The meteorite of Bishopville, South Carolina, was found on microscopic examination to consist of the following minerals: enstatite, feldspar, monoclinic pyroxene, olivine, pyrrhotine, and nickel-iron. The enstatite contains many glass inclusions, microliths, chromite and metallic grains. The feldspar is mostly plagioclase, with exceedingly fine twinning bands. It contains numerous yellowish-brown, dark, or almost colourless inclusions, and minute crystals of enstatite in rosette-like forms. In its mineralogical composition and its structure the meteorite resembles gabbro (norite).

The doubtful meteorite of Waterville, Maine, proves to be a laminated ash-grey, cellular, cinder-like slag, consisting of a cellular, glassy mass, which has begun to devitrify, and has been long exposed to the action of atmospheric agencies.

B. H. B.

**The Alfanello Meteorite.** By H. v. FOULLON and W. FLIGHT (*Jahrb. f. Min.*, 1884, **2**, Ref., 30—32).—This meteorite has already been described in detail (*Abstr.*, 1883, 1071).—I gives the results of Foullon's analysis of material from six specimens; II, the composition of the portion soluble in acid; III, that of the insoluble silicates. IIa and IIIa give the results obtained by Flight:—

	I.	II.	IIa.	III.	IIIa.
SiO <sub>2</sub> . . . .	39·14	35·05	35·12	56·22	56·12
Al <sub>2</sub> O <sub>3</sub> . . . .	0·93	0·41	1·52	1·64	[Cr <sub>2</sub> O <sub>3</sub> = 8·28]
FeO . . . .	17·42	28·53	51·43	12·16	13·40
CaO . . . .	1·96	0·55	4·64	4·16	6·71
MgO . . . .	25·01	35·46	7·27	23·76	17·26
Na <sub>2</sub> O . . . .	0·75	—	—	} 2·06	—
K <sub>2</sub> O . . . .	0·10	—	—		
Fe . . . . .	11·31	—	—	—	—
Ni . . . . .	1·09	—	—	—	—
S . . . . .	2·71	—	—	—	—
Totals . . .	100·42	100·00	99·28	100·00	101·77

From these results the mineralogical composition is calculated (IV) by Foullon, and (V) by Flight.

IV.		V.	
Bronzite and felspar..	41·37	Insoluble silicates ..	40·12
Olivine .....	43·77	Soluble silicates....	50·86
Nickel iron .....	7·66	Nickel iron.....	2·11
Magnetic pyrites ....	7·45	Troilite .....	6·92

The results given under II and IIa, III and IIIa, do not agree very well, and the high percentage of chromium in IIIa is especially remarkable. In the analysis IIIa, the percentage of silica is also too high for an olivine so rich in iron.

B. H. B.

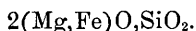
**The Rowton and Middlesbrough Meteorites.** By W. FLIGHT (*Jahrb. f. Min.*, 1884, 2, Ref., 28—30).—The iron meteorite of Rowton is the first whose fall has been observed in Great Britain. It took place on April 20th, 1876, at 3.40 p.m. Analysis I gives the composition of the nickel iron; II, that of the troilite. The iron yielded 6·38 times its volume of gas, an analysis of which is given (III):—

I.		II.		III.	
Fe ....	91·15	Fe ....	63·93	CO <sub>2</sub> ....	5·15
Ni ....	8·67	S ....	36·07	H ....	77·78
Co ....	0·34			CO....	7·34
Cu....	trace			N ....	9·72

The Middlesbrough meteorite fell on the 14th of March, 1881, at 3.35 p.m. The sound resembled the boom of a gun, but no luminous or cloud-forming phenomena are reported. The stone weighed 3 lb. 8½ oz., and forms a low pyramid. It has a greyish-white colour, and is for the most part composed of silicates. The metallic particles (9·38 per cent.) obtained by treating with mercuric chloride gave on analysis the following results:—

Fe.	Ni.	Co.	Total.
76·99	21·32	1·69	100·00

Of the remaining constituents 59·94 per cent. were soluble silicates (Analysis II), and 40·06 per cent. insoluble (Analysis III). The analysis of the soluble portion indicates the presence of



No lime and no alumina were found. The insoluble portion is bronzite, or, as is more probable, augite with labradorite.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Total.
II.	41·10	—	27·96	—	30·94	100·00
III.	55·39	4·77	23·58	4·37	11·04	99·15

B. H. B.

**The Nogoya Meteorite.** By WEBSKY and DAUBRÉE (*Jahrb. f. Min.*, 1884, 2, Ref., 32).—The meteorite fell at Nogoya, in the Argentine Republic, in the winter of 1880, with distinct luminous phenomena. The form is that of a spheroid, 15—18 cm. in diameter. The



weight is  $4\frac{1}{2}$  kg. It belongs to the carbonaceous meteorites, and resembles most closely that of Cold Bokkeveld. B. H. B.

**Mineral Water from Aruba.** By D. DE LOOS (*Ber.*, 17, 999).—This mineral water, from Antikroeri, in the West Indian island of Aruba, has been analysed, and found to contain no copper salts, as was supposed. One litre of the water contains 11.16 grams mineral salts, of which 2.13 grams are magnesium chloride, and the remainder chlorides and sulphates of the alkalis, along with a little calcium sulphate. A. B.

**Composition of Borhegyer Water.** By M. BALLO (*Ber.*, 17, 673—674).—This mineral water, from the vicinity of Bibarczfalva, in the Siebenbürgen, contains in grams per litre:—

Calcium carbonate .....	0.65040
Magnesium carbonate .....	0.42075
Sodium carbonate .....	0.37489
Lithium carbonate .....	0.00646
Ferrous carbonate .....	0.07428
Manganous carbonate .....	0.01824
Potassium sulphate .....	0.00034
Sodium chloride .....	0.10971
Potassium chloride .....	0.05820
Sodium bromide .....	0.00046
Sodium iodide .....	0.00018
Alumina .....	0.00952
Phosphoric acid .....	traces
Silica .....	0.08454
	<hr/>
	1.80797
Total carbonic anhydride .....	3.13008
Carbonic acid present as bicarbonates .....	1.4023
Free carbonic anhydride .....	1.72778

A. J. G.

### Organic Chemistry.

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**Monobromomethyl Chloroform (Bromotrichlorethane).** By L. HENRY (*Compt. rend.*, **98**, 370—372).—This compound,  $\text{CCl}_3\text{CH}_2\text{Br}$ , may be obtained by heating the trichlorethane,  $\text{CCl}_3\text{CH}_3$ , with bromine at  $150\text{--}160^\circ$  in sealed tubes, but higher brominated derivatives are formed at the same time. It is more conveniently prepared by the action of antimony pentachloride on  $\text{CCl}_2\text{Br}\cdot\text{CH}_2\text{Br}$  or  $\text{CClBr}_2\cdot\text{CH}_2\text{Br}$ . It is a colourless mobile liquid of ethereal odour boiling at  $151\text{--}153^\circ$

Its sp. gr. at 0° is 1·8839. When treated with alcoholic potash, it is decomposed, the elements of hydrochloric acid being eliminated and the compound  $\text{CCl}_2 : \text{CHBr}$  formed; this is a colourless liquid which boils at 114—116°. It has a powerful odour and rapidly absorbs oxygen on exposure to the air.

The following table gives the properties of the chlorinated brom-ethanes:—

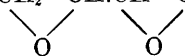
	B. p.	Density.
$\text{CH}_2\text{Br}.\text{CH}_3$ . . . . .	38°	1·4733
$\text{CH}_2\text{Br}.\text{CH}_2\text{Cl}$ . . . .	108	1·7387
$\text{CH}_2\text{Br}.\text{CHCl}_2$ . . . .	138	1·8587
$\text{CH}_2\text{Br}.\text{CCl}_3$ . . . . .	151	1·8839

C. E. G.

**Propargyl Iodide.** By L. HENRY (*Ber.*, **17**, 1132—1133).—Propargyl iodide, prepared by the action of sodium iodide on propargyl bromide in alcoholic solution, is a pale-yellow liquid boiling at 115°, sp. gr. at 0° 2·0177, non-miscible with water. It unites with mercury forming a yellow crystalline compound,  $\text{C}_3\text{H}_3\text{HgI}$ , and with iodine, yielding propargyl triiodide,  $\text{C}_3\text{H}_3\text{I}_3$ , which is deposited from a warm ethereal solution in colourless needles melting at 40°. An addition-product of the composition  $(\text{C}_3\text{H}_3\text{I}_2)_2\text{HPO}_2$  is formed by the action of iodine and amorphous phosphorus on propargyl alcohol (*Ann. Soc. scientifique Bruxelles*, 1878).

W. C. W.

**Second Anhydride of Erythrol,  $\text{C}_4\text{H}_6\text{O}_2$ .** By S. PRZYBYTEK (*Ber.*, **17**, 1091—1096).—This dioxide has been obtained by the action of potassium hydroxide on erythrol dichlorhydrin, and is a complete internal anhydride of erythrol as shown by the formula  $\text{CH}_2-\text{CH}.\text{CH}-\text{CH}_2$ . Erythrol dichlorhydrin, melting at 124°, was



prepared by the action of concentrated hydrochloric acid on erythrol at 100°. The dichlorhydrin was dissolved in ether, and powdered potassium hydroxide added as long as any reaction took place; this reaction was observed by the precipitation of potassium chloride and the slight boiling of the ether. After the separation of the precipitate, the ether was evaporated off, and the new oxide distilled. It is a colourless mobile liquid boiling at 138°, and has a disagreeable peculiar odour and a burning taste. The sp. gr. at 0° is 1·1322, at 18° 1·1132. It is extremely volatile, passing over with the vapour of ether.

Analysis leads to the formula  $\text{C}_4\text{H}_6\text{O}_2$ . The estimation of the vapour-density by Meyer's method with aniline vapour gave it as 3·12—3·20, whilst that calculated for  $\text{C}_4\text{H}_6\text{O}_2$  is 2·91.

The chemical properties of this compound show that it has the above constitutional formula. It combines with water, acids, and ammonia, to form addition-products in the proportion of 1 mol. to 2 mols. water or 2 mols. monobasic acid. It mixes in all proportions with water, and combines with it to form erythrol, somewhat slowly at the ordinary temperature, more quickly at 100°. Hydrochloric acid

converts it into the original dichlorhydrin. It combines with dry hydrocyanic acid at  $50-55^{\circ}$  to form the nitrile of dihydroxyadipic acid,  $C_6H_8(OH)_2(CN)_2$ . When heated with 2 mols. hydrocyanic acid at  $50-55^{\circ}$  for four or five hours, it forms an amorphous mass of nitrile, and this when treated with potash gives ammonia, and is converted into the potassium salt of dihydroxyadipic acid. The capacity of this oxide to combine with acids is so strong that it will precipitate magnesia and cupric oxide from their soluble salts. With ammoniacal silver nitrate, it gives a silver mirror. It combines with 2 mols. of aniline to form an addition-product,  $C_{16}H_{20}N_2O_2$ , insoluble in water and ether, and combining with mineral acids to form salts. The hydrochloride of this aniline compound,  $C_{16}H_{20}N_2O_2 \cdot 2HCl$ , forms large colourless plates. The same salt can be obtained by heating the dichlorhydrin with aniline at  $100^{\circ}$ .

The properties of this oxide are analogous to those of the series  $C_nH_{2n}O$ . It is the first member of a series of dioxides which would have the general formula  $C_nH_{2n-2}O_2$ . The author is at present engaged in preparing the dichlorhydrin,  $C_6H_{12}O_2Cl_2$ , by the action of hypochlorous acid on diallyl, and hopes to obtain a dioxide from it by the action of potassium hydroxide.

A. B.

**Lactose and Mucic Acid.** By W. H. KENT and B. TOLLENS (*Ber.*, 17, 668).—In preparing lactose from milk-sugar, hydrochloric acid gives better results than sulphuric acid. The action of nitric acid in systematically increased amounts on milk-sugar and on lactose has been investigated. In favourable cases there has been obtained from milk-sugar 38 per cent., and from lactose 77 per cent. of mucic acid. 10–15 per cent. solutions of lactose show a rotary power  $[\alpha]_D = 81.4-81.7^{\circ}$ . Lactose yields lævulinic acid when heated with hydrochloric acid.

A. J. G.

**Lactosin: a New Carbohydrate.** By A. MEYER (*Ber.*, 17, 685—692).—Lactosin is a crystalline carbohydrate occurring largely in the Caryophyllacæ, in which it plays the same part as inulin in the Compositæ. It is best prepared from the roots of *Silene vulgaris*, those gathered in autumn being richest in lactosin. The grated roots are pressed, the juice mixed with an equal volume of alcohol (95 per cent.), and allowed to stand twelve hours; the precipitated proteids are then filtered off, the filtrate mixed with an amount of alcohol equal to three times the original volume of the juice, and allowed to stand 24 hours. The precipitate is dissolved in a little water and again precipitated with alcohol; the crude lactosin so obtained still contains 2.1 per cent. of ash. It is best purified by precipitation from aqueous solution by lead acetate and ammonia; the sparingly soluble lead compound is decomposed by hydrogen sulphide, the aqueous solution concentrated, and, whilst still hot, precipitated by alcohol; the precipitate is dissolved in water, evaporated on the water-bath, and dried over sulphuric acid. Amorphous lactosin so obtained is free from ash, and shows all the properties of the crystalline form, except that the specific rotation  $= +168^{\circ}$ . Probably lactosin exists in two

modifications mainly distinguished by the difference in their rotary powers.

*Crystalline lactosin* is prepared from the amorphous form by boiling it for some days in a vessel provided with a reflux condenser with an amount of alcohol of 80 per cent. insufficient for complete solution. It forms small colourless, lustrous crystals of the formula  $C_{36}H_{62}O_{31} + H_2O$ , loses its water on long heating at  $100^\circ$ , and has the specific rotation  $[\alpha]_D = +211.7^\circ$ . It is moderately soluble in water, the colourless solution resembles an aqueous solution of dextrin in its physical properties, is not precipitated by lead acetate, basic lead acetate, or lime-water, but is precipitated by lead acetate and ammonia. It does not reduce Fehling's solution of the ordinary strength, but appears to exert a slight reducing action on weak solutions. An alcoholic solution is precipitated by basic lead acetate and by lime-water, but not by normal lead acetate. Addition of alcoholic potash or soda precipitates the potassium or sodium derivatives of lactosin.

On inversion, lactosin yields lactose and a sugar of rotary power equal to about  $+17^\circ$ , whose investigation will be continued.

A. J. G.

### **Gallisin, the Unfermentable Part of Commercial Glucose.**

By C. SCHMITT and A. COBENZL (*Ber.*, 17, 1000—1015).—Neubauer and other authors have stated that in wine, which in its preparation has been subjected to Gall's treatment with glucose and fermented, a certain portion of the glucose remains in the wine as an unfermented substance which is neither glucose nor dextrin. Owing to the interest that has arisen as to the possible unwholesomeness of gallinated wines, the authors have been led to investigate the subject, and have succeeded in separating from fermented glucose (prepared from potato-starch) an intensely hygroscopic substance which they have named *gallisin*. A physiological investigation of this compound is in progress, but at present for purposes of priority, the purely chemical part of the research is published.

*Preparation of Gallisin*.—A solution of 5 kilos. of glucose was fermented at  $18-20^\circ$  for five or six days with yeast and filtered. The solution thus obtained was then evaporated to a thick syrup on the water-bath and shaken in a flask with a large excess of absolute alcohol: it became thicker, but did not mix with the alcohol. After a second treatment with absolute alcohol (by means of which water, sugar, organic acids, &c., are extracted) the syrup was found to be converted into a crumbling yellow-gray mass, which by pounding in a mortar with a mixture of absolute alcohol and ether can be obtained as a gray powder. This powder may be purified by dissolving it in water, repeating the above treatment, and drying over sulphuric acid.

*Gallisin* when viewed under the microscope is found to be amorphous and without any characteristic structure. It is intensely hygroscopic, more so than calcium chloride, but yields no definite compound with water. It is insoluble in ether, chloroform, and benzene, very sparingly soluble in glacial acetic acid and in absolute alcohol, but slightly more so in methyl alcohol, and in this it differs from glucose which is readily soluble. It dissolves when boiled in a mixture of

glacial acetic acid and absolute alcohol, but it is precipitated from this solution by ether. In concentrated aqueous solution, it has an acid reaction to litmus-paper; and undergoes no change, either by heat or when treated with lead acetate, mercuric nitrate or chloride, ferric chloride, tincture of iodine, or calcium or barium chloride. Barium hydroxide precipitates a small quantity of a white barium compound. With silver nitrate, it undergoes no change until it is heated or ammonia is added, when metallic silver is precipitated. It rapidly reduces potassium permanganate, especially in slightly alkaline solution, with separation of peroxide of manganese. Potassium dichromate in dilute acid solution is also rapidly reduced. Fehling's and Knapp's solutions are reduced by it (in this it differs from dextrin), and 0.05 g. glucose are equal to 0.109784 g. gallisin in reducing power. A concentrated solution of gallisin prevents the precipitation of iron salts by ammonia or caustic alkalis. With acetic anhydride, it gives an acetyl compound, and it is converted into glucose by treatment with dilute mineral acids on the water-bath. On treating an aqueous solution with fresh yeast it is not fermented, nor does it undergo lactic fermentation, but if a dilute aqueous solution is allowed to stand for a time it decomposes with formation of a mouldy fungus. At 100° it gives off water and carbonic anhydride. It has a slightly sweet taste at first, but in time becomes insipid. A solution of gallisin turns the plane of polarisation to the right, and this power increases according to the dilution of the solution. A very pure white specimen, when analysed with every care to prevent access of moisture, was found to contain 43.50 per cent. C and 7.36 per cent. H, and these results lead to the formula  $C_{12}H_{24}O_{10}$  (C, 43.9 : H, 7.32).

*Gallisin-barium*,  $C_{12}H_{22}BaO_{10} + 3H_2O$ , may be obtained by precipitating a concentrated aqueous solution of gallisin by barium hydroxide in alcoholic solution, and is purified by dissolving the precipitate in water, reprecipitating with alcohol, and washing with ether. The pure substance readily absorbs carbonic anhydride, is slightly alkaline, and reduces Fehling's and Knapp's solutions. It loses its water of combination over sulphuric acid.

*Hexacetylgallisin* is formed by heating gallisin with acetic anhydride for two and a half hours at 130—140° under pressure. The resulting brown mass is soluble in alcohol, and after driving off the excess of acetic anhydride on the water-bath, may be purified by boiling with charcoal; the acetyl-derivative is obtained on evaporation of its alcoholic solution as a colourless glass-like mass of the formula  $C_{12}H_{18}O_{10}Ac_6$ . It is insoluble in water, but soluble in alcohol and similar solvents. If gallisin be heated for several hours at 170—180° with an excess of acetic anhydride, it is decomposed with formation, amongst other products, of ethyl acetate.

*Gallisin-potassium*,  $C_{12}H_{23}KO_{10}$ , is precipitated from an alcoholic solution of hexacetylgallisin by boiling it with alcoholic potash, ethyl acetate being formed simultaneously. It is a hygroscopic powder soluble in water, with alkaline reaction. In a similar way a precipitate of gallisin-lead may be obtained,  $C_{12}H_{22}PbO_{10} + PbO$ .

*Conversion of Gallisin into Grape-sugar*.—Equal parts by weight of gallisin and oxalic acid were heated on the oil-bath at 103° for two to

three hours. On separating the oxalic acid with lime and evaporating the solution, a thick sweet syrup was obtained which in a few days formed a crystalline mass of glucose. The whole of the gallisin, however, could not be converted into glucose: by the prolonged action of oxalic acid on an aqueous solution of gallisin, it becomes yellow, and smells strongly of caramel.

*Oxidation of Gallisin.*—On pouring a solution of 100 grams gallisin in 50 c.c. water into 400 grams strong nitric acid, a powerful reaction takes place, and the solution becomes heated to boiling, with evolution of nitrous fumes. On cooling, neutralising with potash, and afterwards strongly acidifying with acetic acid, an acid potassium salt crystallises out in beautiful groups of white needles soluble in hot water but sparingly in cold. About 20 grams of these were obtained and the results of analysis agreed with the formula  $C_6H_9KO_8$ . From this acid salt a neutral silver salt,  $C_6H_8Ag_2O_8$ , was prepared, and from the lead salt by the action of sulphuretted hydrogen the free acid was obtained as a thick, acid, uncrystallisable syrup, soluble in water and alcohol but insoluble in ether. On distilling the ammonium salt, besides ammonia, pyrroline, &c., a sublimate was obtained which is soluble in water, alcohol, and ether, and at present is under investigation.

*Action of Heat on Gallisin.*—On heating gallisin in a current of hydrogen gas on the water-bath at  $65^\circ$ , carbonic anhydride and water are given off, and at  $100^\circ$  it melts to a thick amber-coloured syrup; 17.2 per cent. of water (4 mols. = 18 per cent.) and 13.7 per cent. of carbonic anhydride (1 mol. = 13.4 per cent.) were given off. This syrup has many of the properties of gallisin, as has also its barium compound, which is found on analysis of the barium derivative to have the formula  $(C_{11}H_{23}O_8)_2Ba$ . This may mean that gallisin, when heated, gives up water and carbonic anhydride, but when the resulting substance is treated with water the water is again taken up, and, as the barium derivative shows, a compound is formed containing 1 mol. of carbonic anhydride less than gallisin.

The authors succeeded also in preparing pure gallisin from a wine which had been prepared by Gall's process in 1873, and identified it by the above reactions and by analysis. In conclusion, the authors mention that a physiological investigation of gallisin is being made, and already it has been found by numerous trials that there is no direct or indirect unwholesomeness in the use of gallisin or of the glucose which is formed along with it.

A. B.

**Invertin.** By E. BOURQUELOT (*J. Pharm. Chim.* [5], 7, 131—134).—Experiments were made in reference to the action of the soluble ferment of yeast (invertin) on gelatinised starch. The invertin was obtained from the yeast now largely used by bakers (brewers' yeast gives a bitterness to the bread), which is prepared by sowing yeast in a mixture of rye or maize meal with malt: this yeast has a little diastase mechanically adhering to it. 50 grams of the yeast were mixed with 100 c.c. of distilled water, and, after standing, the solution was filtered. The residual yeast was treated with water in this way four times in succession. The four solutions were all found to be rich in invertin, indicated by its hydrolytic action on

cane-sugar. Berthelot and Bechamp have previously shown that yeast furnishes large quantities of invertin to water when isolated from nutrient matter. The above liquids were allowed to act for some hours on gelatinised starch, after which it was found by testing with iodine that the first solution alone exercised a hydrolytic action on the starch, and this only to a feeble extent, which the author supposes is due to adherent diastase; the other liquids had no action on the starch. The author therefore concludes that invertin, unlike diastase, has no hydrolytic action on starch.

W. R. D.

**Direct Conversion of Alcohols of the Ethyl Series into Amines.** By V. MERZ and K. GASIOROWSKI (*Ber.*, **17**, 623—640).—Although it is known that phenols when heated with ammonia, best in presence of dehydrating agents, are converted into primary and secondary amines, the reaction has not yet been worked out with alcohols of the ethyl series. Ammonia alone has no action, and but slight action in presence of calcium chloride; good yields were obtained only in the presence of zinc chloride at high temperatures.

Methyl alcohol, heated in sealed tubes at 200—220° for 16 hours with the compound of zinc chloride and ammonia, yields mono- and tri-methylamine. The formation of dimethylamine also was highly probable, although it was not proved.

Absolute alcohol and ammonio-zinc chloride react but slightly at 200—220°; on further heating for eight hours at 260°, mono-, di-, and tri-ethylamine are formed, the yield of mixed amines being about 50 per cent. of the alcohol employed. Ethylene and pyridine bases appear also to be formed.

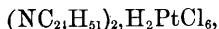
Isobutyl alcohol and ammonio-zinc chloride react but slightly at 200—220°, even after being heated for 16 hours; at 260—280° from 50—75 per cent. of the alcohol is converted into amines. Mono-, di-, and tri-isobutylamine were isolated from the product. Isobutyl alcohol and ammonium chloride react but slightly at 280°.

Normal octyl alcohol and ammonio-zinc chloride on being heated at 280° for 16 hours give a large yield of amines (over 75 per cent. of the alcohol used). Monoctylamine has been described by Eichler (*Abstr.*, 1880, 229). *Diocetylamine*,  $\text{NH}(\text{C}_8\text{H}_{17})_2$ , crystallises in long white needles having an odour like that of tallow. It melts at 36.5°, boils at about 297—298°, is practically insoluble in water, readily soluble in alcohol and ether. The *hydrochloride*,  $\text{NH}(\text{C}_8\text{H}_{17})_2\text{HCl}$ , crystallises in colourless plates, is sparingly soluble in water or ether, soluble in alcohol. The *platinochloride*,  $[\text{NH}(\text{C}_8\text{H}_{17})_2]_2\text{H}_2\text{PtCl}_6$ , forms clear yellow plates practically insoluble in water. *Triocetylamine*,  $\text{N}(\text{C}_8\text{H}_{17})_3$ , after long purification forms a white crystalline mass, but was usually obtained as a nearly colourless oil of agreeable ethereal odour. It boils at 365—367°, is readily soluble in ether and absolute alcohol, but very sparingly soluble in ordinary spirit. Most of its salts are liquid. The *platinochloride*,  $(\text{NC}_8\text{H}_{17})_3\text{H}_2\text{PtCl}_6$ , forms a glutinous mass insoluble in water.

In order to ascertain the nature of the reaction in the case of a secondary alcohol, capryl alcohol was heated with ammonio-zinc chloride. The yield of amines was much less than with the primary



alcohols, being only about 25 per cent. of the weight of the alcohol employed. Monocaprylamine has long been known. *Dicaprylamine*,  $\text{NH}(\text{C}_8\text{H}_{17})_2$ , forms a colourless oil of aromatic odour. It boils at about  $270^\circ$ ; vapour-density = 8.49 (calc. 8.33). The *hydrochloride* is a white crystalline substance soluble in alcohol. The *platinochloride*,  $(\text{NC}_{16}\text{H}_{35})_2\text{H}_2\text{PtCl}_6$ , crystallises in fine yellow plates; the *aurochloride*,  $\text{NC}_{16}\text{H}_{35}\text{HAuCl}_4$ , crystallises in golden-yellow plates. *Tricaprylamine* is also an oil of aromatic odour. It boils a little above the boiling point of mercury. The *platinochloride*,



was obtained as a compact resinous mass showing slight signs of crystallisation.  
A. J. G.

**Action of Zinc-ethyl on Amines and Phosphines.** By H. GAL (*J. Pharm.* [5], 7, 484—485).—Zinc-ethyl has been found by the author to be without action on tertiary amines, while it acts violently on primary and secondary amines, the unsubstituted hydrogen being replaced by zinc with disengagement of ethane. The same appears to be the case with the phosphines. The bodies used in these experiments were triethylamine, dimethylphenylamine, methyl-diphenylamine, and trimethylphosphine, all of which were unacted on by zinc-ethyl. The author proposes to utilise this reaction for the diagnosis of primary, secondary, and tertiary amines. The body is mixed with zinc-ethyl in ethereal solution to moderate action, when the amines of the first two classes will give rise to a reaction in which ethane is continuously and regularly evolved, while the tertiary amines will be unacted on. The action of zinc-ethyl on alkaloids was also examined. No reaction occurred with nicotine or with quinoline; hence these bases contain no hydrogen which is replaceable by zinc. The alkaloids that contain oxygen were generally attacked, yielding metallic derivatives, which were easily isolated. These new compounds are only slowly altered by exposure to the air, but are rapidly decomposed by water, forming zinc oxide and regenerating the alkaloid; they form crystalline salts with sulphuric and hydrochloric acids.  
W. R. D.

**Glyoxalisoamyline and its Derivatives.** By B. RADZISZEWSKI and L. SZUL (*Ber.*, 17, 1291—1296).—Radziszewski has already described (*Abstr.*, 1883, 1086) the preparation of glyoxalisoamyline from glyoxal and the ammonio-compound of isovaleraldehyde. The authors now find that it may be obtained by passing a current of dry ammonia into a mixture of crude glyoxal and isovaleraldehyde in alcoholic solution. Care must be taken not to allow the temperature to rise to any extent during the reaction. The *hydrochloride* is a colourless deliquescent body crystallisable from alcohol with difficulty, and melting at  $135$ — $136^\circ$ . The *hydrobromide* is similar in properties, and melts at  $100^\circ$ . The *sulphate* is so deliquescent that it could not be obtained pure, but is a neutral sulphate. The *oxalate* was obtained in fine rhombic crystals having the axial relations  $a : b : c = 0.4784 : 1 : 0.4603$ .

If bromine be gradually added to an ethereal solution of glyoxalisoamyline at  $0^{\circ}$  until it is no longer *completely* decolorised, the product yields glyoxalisoamyline hydrobromide and dibromoglyoxalisoamyline. The weight of bromine added then equals the weight of the glyoxalisoamyline employed. If three times this quantity of bromine be added the liquid remains of an orange colour, and dibromo- and tribromoglyoxalisoamyline are obtained, together with a good deal of resinous matter not investigated.

*Dibromoglyoxalisoamyline* crystallises in colourless scales melting at  $157-158^{\circ}$ , and with silver nitrate gives a white precipitate, which rapidly turns black on exposure to the light, and decomposes at  $300^{\circ}$  without previous fusion. *Tribromoglyoxalisoamyline* crystallises from alcohol in colourless needles, which blacken at  $200^{\circ}$  and melt at  $216-217^{\circ}$ . It is soluble in alcohol and ether, and sparingly so in water. It is converted into the dibromo-compound when treated in aqueous solution with sulphurous acid; it also gives up a third of its bromine to silver nitrate. *Oxalmethyloisoamyline* was obtained by the action of glyoxalisoamyline on methyl iodide, but in quantity too small for investigation. Its *methiodide*,  $C_7H_{11}MeN_2, MeI$ , was obtained in rhombic prisms. When heated to  $136^{\circ}$ , the crystals from an alcoholic solution lose their transparency, and melt at  $169-170^{\circ}$ ; the crystals from an aqueous solution do not show this loss of transparency.

*Oxalethylisoamyline* was obtained by the action of ethyl bromide on glyoxalisoamyline. It forms a colourless liquid of unpleasant pungent odour, boils at  $224-225^{\circ}$  ( $B. = 743$  mm.,  $t_B = 19.4^{\circ}$ ); its sp. gr. is 0.9291 at  $19.6^{\circ}$ . The *platinochloride* crystallises in orange-coloured prisms, soluble in hot water.

*Oxalpropylisoamyline* is a colourless liquid, boiling at  $239-242^{\circ}$  ( $B. = 738$  mm.,  $t_B = 23^{\circ}$ ). It is more sparingly soluble in water than the ethyl compound, and its sp. gr. is 0.9149 at  $18^{\circ}$ . The *platinochloride* is soluble in alcohol and boiling water, and crystallises in microscopic prisms. Oxaldipropylisoamyline bromide, simultaneously formed, crystallises in colourless prisms, belonging to the rhombic system, soluble in water and alcohol, and melting at  $162-163^{\circ}$ . With silver nitrate, it gives a precipitate of silver bromide.

*Oxalisobutylisoamyline*,  $C_7H_{11}(\beta Bu)N_2$ , boils at  $238-242^{\circ}$  ( $B. = 742$  mm.,  $t_B = 18^{\circ}$ ), and has a sp. gr. of 0.9048 at  $16.1^{\circ}$ . The *platinochloride* crystallises in golden-coloured scales.

*Oxalisoamyloisoamyline* boils at  $261-262^{\circ}$  ( $B. = 737$  mm.,  $t_B = 19^{\circ}$ ), is insoluble in water, and has a sp. gr. of 0.9029 at  $14.9^{\circ}$ . The *platinochloride* forms minute crystals. A double salt with zinc chloride forms very hygroscopic white crystals melting at  $86-87^{\circ}$ . Oxidised with hydroxyl, oxalisoamyloisoamyline yields isoamyloxamide.

The action of these oxalines with tannic, picric, and tungstic acids, &c., is similar to that of those already described. L. T. T.

**Oxidation of Oxalines and Glyoxalines by means of Hydroxyl.** By B. RADZISZEWSKI (*Ber.*, 17, 1289-1290).—Trommsdorff now supplies a 3 per cent. solution of pure hydroxyl, which the author finds a very convenient oxidising agent.

Wyss found that glyoxaline treated with the ordinary oxidising

agents yields only carbonic anhydride and traces of formic acid. The author dissolved glyoxaline in an alkaline solution of hydroxyl; oxygen was liberated, and the mixture was then allowed to remain for several days undisturbed: on examination, it was then found to contain oxamide and apparently traces of oxamic acid. Glyoxal-ethyline and glyoxalpropyline similarly treated also yielded oxamide, the yield of the latter body increasing with the molecular weight of the original substance.

Glycocine,  $C_6H_8N_4$ , in sulphuric acid solution, when treated with hydroxyl yields dark violet and black colouring matters, which are insoluble in the ordinary solvents, and are now being investigated. All the oxalines give substituted oxamides with hydroxyl: for instance, oxalethylpropyline and oxalethylethyline both yield ethyl-oxamide, whilst oxalisomylymyline yields isomyloxamide.

L. T. T.

### Diazo- and Diazoamido-derivatives of the Paraffin Series.

By T. CURTIUS (*Ber.*, 17, 953—959).—In this preliminary notice, the author confirms his observation (*Abstr.*, 1884, 42) that by the action of sodium nitrite on ethylic glycocine hydrochloride an ethylic diazoacetate is formed—that is, a compound in which two hydrogen atoms of the methyl group in the acetic acid part, are replaced by a double atom of triad nitrogen. This reaction seems to be general in cases in which a hydrochloride of the ethereal salt can be formed, and has been successful with alanine, tyrosine, leucine, amidomalonic acid, and aspartic acid.

*Ethylic glycocine nitrite* is easily formed by suspending ethylic glycocine hydrochloride in ether, adding finely powdered silver nitrite, and separating the resulting silver chloride with alcohol. When the alcoholic solution of the nitrite is evaporated in a vacuum over sulphuric acid, it yields large colourless crystals of the formula  $NOOH.NH_2.CH_2.COOEt$ . In time, or more quickly at  $50^\circ$ , or by distillation in steam, water separates out, and the diazo-compound is formed. The comparative stability of this compound is a proof that the nitrogen-atoms are both united to carbon. In small quantities (2—3 grams) it can be distilled, but with larger quantities explosion takes place. The yield is about 80 per cent. of the theoretical quantity.

*Ethylic diazoacetate*,  $(N_2CH.COOEt)$  gives on boiling with benzoic, hippuric, or glacial acetic acids respectively benzo-, hippuro-, or aceto-ethylic glycollate. Chlorine in the cold converts it into ethylic dichloroacetate with separation of nitrogen. The reactions with bromine and iodine are similar. Hydrochloric acid in aqueous solution converts it into ethylic monochloroacetate and ethylic glycollate. Hydrofluoric acid in aqueous solution converts it only into ethylic glycollate or ethylic diglycollate, according to the quantity of water used. With hydrofluoric acid, however, it yields ethylic fluoacetate. This reaction, and also those of nitric, nitrous, and chlorous acids, are under further investigation. On heating it with benzaldehyde, and acting on the oily product with dilute soda, phenylacetic acid is formed with the separation of a carbon-atom. With benzamide no ethylic hippurate was formed as was expected, but a crystalline sub-

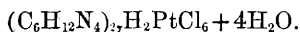
stance melting at about  $95^{\circ}$ , and now under investigation. Hydrocarbons such as toluene have no action on it, even on boiling. As it is undecomposed by acetic acid at  $60^{\circ}$ , it was found possible to reduce it with zinc and acetic acid to ethylic hydrazine acetate, the hydrochloride of which is unstable. This compound reduces Fehling's solution in the cold, and on being evaporated with hydrochloric acid rapidly decomposes into glycocine hydrochloride and ammonium chloride. Potassium and sodium dissolve in ethylic diazoacetate with evolution of hydrogen, and form brown precipitates, which are also under further investigation.

On passing the gases obtained by oxidising arsenic trioxide with nitric acid through a solution of ethylic glycocine in ether, at first no diazoacetate is formed, but a thick orange-coloured oil, insoluble in ether, and seemingly having the properties of a diazoamido-compound. It has not yet, however, been obtained in a pure state. Ethylic diazoacetate, when slowly dissolved in concentrated aqueous ammonia, yields a yellow crystalline mass melting at  $97^{\circ}$ ; this appears to be a diazoacetamide.

The amido-acids of the fatty series do not form diazo-compounds unless the hydrogen of the acid hydroxyl is replaced by an alcohol radical, nor does the acid ether of a dibasic acid. Ethylic aspartic acid gives no diazo-compound, although it forms a stable hydrochloride; ethylic aspartate, on the other hand, yields ethylic diazosuccinate.

A. B.

**Derivatives of Formaldehyde.** By B. TOLLENS (*Ber.*, **17**, 653—659).—A continuation of the author's work on this subject. *Hexamethylenamine* can be conveniently prepared by evaporating a mixture of ammonia and crude formaldehyde. It is stable in the air, readily soluble in water, more sparingly in alcohol. When heated at  $230$ — $270^{\circ}$  in a vacuum, it sublimes without decomposition. Attempts to determine the vapour density were unsatisfactory, the numbers obtained being 3.809 and 3.889; calculated, 4.86 for  $C_6H_{12}N_4$  and 2.43 for  $C_3H_4N_2$ . The author has further examined the platinochloride. It crystallises in microscopic octohedrons, and has the formula,



Hexamethylenamine is decomposed by acids into formaldehyde or oxymethylene and ammonium salts. Sodium amalgam appears to be without action on it. Heated with methyl iodide, methyl alcohol, and water at  $170$ — $200^{\circ}$ , a considerable amount of tetramethylammonium iodide is formed.

*Anhydroformaldehydaniline*,  $PhN:CH_2$ , is prepared by mixing crude formaldehyde (85 grams) with aniline (5—6 grams), and allowing it to remain at rest for some hours, when the new substance crystallises out. It forms a mass of fine, silky, white needles or plates, which cannot be fused without decomposition. It is readily soluble in chloroform, benzene, and toluene, soluble in ether, very sparingly in alcohol, and almost insoluble in water. It is decomposed by boiling with alcohol or water. Dilute acids scarcely dissolve it, but with concentrated acids it dissolves to a red or brown coloured liquid. Toluidine yields an analogous crystalline compound with

formaldehyde; methylaniline gives an oil and carbamide yields a solid sparingly soluble derivative. A. J. G.

**Action of Baryta on Acetaldehyde. Aldehyde-gum.** By B. TOLLENS (*Ber.*, **17**, 660—661).—By the action of aqueous baryta on acetaldehyde there is obtained, in addition to much aldehyde-resin, a yellow gum-like substance of the formula  $C_{10}H_{18}O_4$ ; it is soluble in alcohol and ether. By treatment with milk of lime, the calcium derivative,  $(C_{10}H_{17}O_4)_2Ca$ , is obtained as a yellowish-white earthy mass, soluble in absolute alcohol, precipitated in flocks by ether. The gum is decomposed by heat, gives a red coloration with the magenta reagent for aldehydes, yields iodoform on treatment with iodine and soda, and reduces Fehling's solution when boiled with it.

A. J. G.

**Potassium and Barium Glyoxal-hydrogen Sulphites.** By DE FORCRAND (*Compt. rend.* **98**, 1537—1539).—*Potassium glyoxal-hydrogen sulphite* is obtained by the same method as the sodium salt (*Compt. rend.*, **98**, 824), and forms brilliant prisms containing  $H_2O$ . The heat of formation was estimated by the first of the methods employed in the case of the sodium salt (*loc. cit.*), and the following results were obtained:—

$C_2H_2O_2$ solid + $2SO_2$ gas + $K_2O$ solid + $H_2O$ solid = $C_2H_2O_2 \cdot 2KHSO_3$ solid.....	develops + 142·81 cal.
$C_2H_2O_2$ solid + $2SO_2$ gas + $K_2O$ solid + $H_2O$ liquid = $C_2H_2O_2 \cdot 2KHSO_3$ solid .....	„ + 144·24 „
$C_2H_2O_2$ + $K_2O \cdot S_2O_4$ solid + $H_2O$ solid = $C_2H_2O_2 \cdot 2KHSO_3$ solid .....	„ + 14·28 „
$C_2H_2O_2$ + $K_2O \cdot S_2O_4$ solid + $H_2O$ solid = $C_2H_2O_2 \cdot 2KHSO_3$ diss. ....	„ + 0·88 „
$C_2H_2O_2$ + $K_2O \cdot S_2O_4$ solid + $H_2O$ liquid = $C_2H_2O_2 \cdot 2KHSO_3$ solid .....	„ + 15·71 „
$C_2H_2O_2$ + $K_2O \cdot S_2O_4$ solid + $H_2O$ liquid = $C_2H_2O_2 \cdot 2KHSO_3$ diss. ....	„ + 2·31 „

The heat of formation of the potassium salt in the solid state is always greater than that of the sodium compound.

*Barium glyoxal-hydrogen sulphite*,  $2(C_2H_2O_2 \cdot BaO \cdot 2SO_2) + 7H_2O$ , is much less soluble than the sodium and potassium salts.

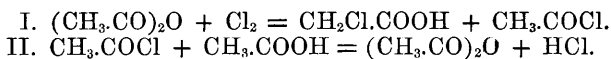
$C_2H_2O_2$ solid + $2SO_2$ gas + $BaO$ solid + $3\frac{1}{2}H_2O$ solid = $C_2H_2O_2 \cdot BaO \cdot S_2O_4 \cdot 3\frac{1}{2}H_2O$ .....	develops + 92·73 cal.
$C_2H_2O_2$ solid + $2SO_2$ gas + $BaO$ solid + $3\frac{1}{2}H_2O$ solid = $C_2H_2O_2 \cdot BaO \cdot S_2O_4 \cdot 3\frac{1}{2}H_2O$ diss. ....	„ + 84·04 „
$C_2H_2O_2$ solid + $2SO_2$ gas + $BaO$ solid + $3\frac{1}{2}H_2O$ liquid = $C_2H_2O_2 \cdot BaO \cdot S_2O_4 \cdot 3\frac{1}{2}H_2O$ solid ....	„ + 97·72 „
$C_2H_2O_2$ solid + $2SO_2$ gas + $BaO$ solid + $3\frac{1}{2}H_2O$ liquid = $C_2H_2O_2 \cdot BaO \cdot S_2O_4 \cdot 3\frac{1}{2}H_2O$ diss. ....	„ + 89·04 „

These results explain the formation of this salt from barium chloride and sodium glyoxal-hydrogen sulphite, and also the precipitation of a solution of the barium salt by dilute sulphuric acid.

C. H. B.

**Action of Carbonic Anhydride on Lead Acetate.** By F. BELLAMY (*J. Pharm.* [5] 7, 216—220).—It is well known that carbonic anhydride acts on a solution of lead acetate with formation of lead carbonate and free acetic acid. In this paper the extent to which the reaction takes place, under different conditions, is investigated. The results show that the quantity of water present does not affect the decomposition, which is usually complete with a 5 per cent. solution after a rapid current of gas has been passing for about two hours and a half. The whole of the lead acetate is never decomposed, the quantity acted on being inversely as the temperature. It is evident from experiments on this point that the acetic acid reacts with the lead carbonate; this occurs slowly if the solution which has been acted on is allowed to stand. The maximum amount of decomposition effected in a solution of lead acetate by carbonic anhydride at a temperature of 7—8° corresponds with 77.48 per cent. of the salt. W. R. D.

**Preparation of Monochloroacetic Acid.** By W. HENTSCHEL (*Ber.*, 17, 1286).—Several kilos. of acetic anhydride are heated at 100° in a suitable tubulated vessel, and a stream of dry chlorine gas passed into the liquid, a slow stream of glacial acetic acid being allowed to flow in at the same time. When the absorption of chlorine slackens the mixture is distilled, and the fraction 180—187° which forms the principal product, collected separately. The reactions are the following:—



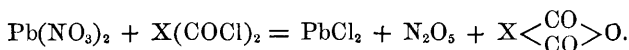
L. T. T.

**Melting Point of Monochloroacetic Acid.** By B. TOLLENS (*Ber.*, 17, 664—667).—Monochloroacetic acid appears to exist in two modifications distinguished by the difference in their fusing points. On taking the melting point of the distilled acid it is found to be 62.5—63.2°, the acid resolidifies at 62—62.5°. When the melting point of the resolidified acid is again determined, it is generally found to be 52—52.5°. If, however, the solidified acid prior to the second fusion is touched with a trace of the crystallised acid, it rapidly assumes an opaque appearance, and now exhibits the original melting point of about 62°. A. J. G.

**Preparation of Acid Anhydrides.** By B. LACHOWICZ (*Ber.*, 17, 1281—1284).—If silver or lead nitrates be acted on by the chlorides of the monobasic acids, the reaction takes place according to the equation—



If the chlorides of the dibasic acids be employed, the reaction is—



As a general rule lead nitrate is to be preferred to silver nitrate, as

the reaction with the latter is generally very violent. As the temperature of reaction lies above the boiling point of some of the lower acid chlorides, and below the melting point of others, the method must be somewhat modified according to circumstances, closed tubes, &c., being used in the one case, and solvents in the other.

The author has prepared acetic, benzoic, and phthalic anhydrides by this method.

L. T. T.

**Preparation of Acid Anhydrides.** By W. HENTSCHEL (*Ber.*, 17, 1285—1286).—If anhydrous sodium acetate be heated to a temperature a little above the boiling point of acetic anhydride, and a rapid stream of phosgene gas be passed over it, acetic anhydride distils over. The anhydride thus prepared has a very unpleasant odour, due to a little phosgene gas dissolved in it, but with a little care can be obtained pure enough for many purposes. Propionic, butyric, and benzoic anhydrides have been prepared in a similar manner. Small quantities of the corresponding chlorides are always present in the anhydrides made in this way.

L. T. T.

**Diacetonylphosphorous Chloride and Diacetonylphosphinous Acid.** By A. MICHAELIS (*Ber.*, 17, 1273—1276).—If aluminium chloride is added to a mixture of 1 vol. phosphorous chloride, and 2—2½ vols. acetone, a brisk reaction takes place, hydrochloric acid is copiously evolved, and the reaction has to be moderated by cooling. From the product a colourless oil is obtained, boiling at 235°, and having the formula  $(\text{CH}_3\text{CO}\cdot\text{CH}_2)_2\text{PCl}$ . *Diacetonylphosphorous chloride* thus obtained has a peculiar but rather pleasant odour; it is heavier than water, and is decomposed by it, slowly in the cold, violently on heating. This aqueous solution, when evaporated on a water-bath, leaves a thick liquid, which solidifies on standing. *Diacetonylphosphinous acid*,  $(\text{CH}_3\text{CO}\cdot\text{CH}_2)_2\text{PH}(\text{OH})_2$ , thus obtained crystallises from water in long colourless needles, containing 1 mol.  $\text{H}_2\text{O}$ , which they lose in a vacuum over sulphuric acid, or at 100—110°. Neutralised with ammonia and treated with silver nitrate, this acid yields a white silver salt of the formula  $(\text{CH}_3\text{CO}\cdot\text{CH}_2)_2\text{PH}(\text{OAg})_2$ , showing that the acid is dibasic. The silver salt is soluble in boiling water, but the solution rapidly decomposes. *Diacetonylphosphinous acid* is a very stable substance, and may be heated to 120° with fuming nitric acid without decomposition. It melts and gives up water at 63—64°. Its solution slowly decolorises bromine-water and potassic permanganate, and with excess of bromine forms bromacetone. It appears to be closely related to Mulder's acetone phosphorus acid,



which the author considers to be most probably monacetonylphosphinous acid,  $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{POH}\cdot\text{OH}$ .

L. T. T.

**Action of  $\alpha\beta$ -Dibromopropionic Acid on Ethyl Malonate.** By M. CONRAD and M. GUTHZEIT (*Ber.*, 17, 1185—1188).—

*Ethyltrimethylenetricarboxylate*,  $\text{CH}_2 \begin{array}{l} \diagup \text{C}(\text{COOEt})_2 \\ | \\ \diagdown \text{CH}\cdot\text{COOEt} \end{array}$ , is formed when

ethyl  $\alpha$ 3-dibromopropionate is added to a mixture of ethyl malonate and sodium dissolved in absolute alcohol. After removing the excess of alcohol by evaporation, the addition of water causes the ethereal salt to separate out as an oily liquid (sp. gr. 1.127 at 15°, b. p. 276°); on saponification, *trimethylenetricarboxylic acid* is obtained in prismatic crystals. A neutral solution of the acid gives white crystalline precipitates with lead and silver salts. The acid melts at 184°, splitting up into carbonic anhydride and *trimethylenedicarboxylic*

acid,  $\text{CH}_2 \begin{array}{l} \diagup \text{CH.COOH} \\ \diagdown \text{CH.COOH} \end{array}$ . The latter compound crystallises in vitreous

prisms, melting at 137°, and soluble in water, alcohol, and ether. The calcium salt is anhydrous. An aqueous solution of the ammonium salt forms white crystalline precipitates with lead acetate and silver nitrate. Trimethylenedicarboxylic anhydride crystallises in glistening needles which melt at 57°. W. C. W.

**Ethyl Glycollate.** By L. MEYER (*Ber.*, 17, 669).—A correction to the results given (*Ber.*, 17, 486). The pressure at which the boiling point of ethyl glycollate was determined was 760 mm., not 730—740 mm. It is very probable that the pressure regulator employed did not act properly. A. J. G.

**Solid Carbonic Acid.** By H. LANDOLT (*Ber.*, 17, 309—311).—For the preparation of solid carbonic acid, the author much prefers the cloth bags which have long been supplied by Bianchi, of Paris, to the ordinary tin boxes. These bags are conical in shape, about 40 cm. long, and about 17 cm. across at the wide end. They are of woollen material, and the wide end can be drawn together by a tape. The narrow end is fastened to a wooden tube which fits over the nozzle of the carbonic acid cylinder. The waste of acid is much less with this bag than with the ordinary box. The solid acid keeps much longer if it be compressed. For this purpose the author uses slightly conical moulds of hard wood, fitted with wooden pistons. Specimens obtained by hammering the solid acid into these moulds have the appearance and approximate hardness of chalk, and may be lightly handled without danger. A specimen 53 mm. long and 71 mm. in diameter took five hours to volatilise. The author finds the average density of his specimens to be slightly under 1.2. L. T. T.

**Existence of the Trimethylene Ring.** By W. H. PERKIN, JUN. (*Ber.*, 17, 323—325).—The author shows that the trimethylenedicarboxylic (ethylenemalonic) acid described by him (*Ber.*, 17, 54) is identical with the vinylmalonic acid obtained by Fittig and Roeder (*Abstr.*, 1883, 730). As the experiments of Fittig and Roeder tend to throw doubt on the existence of a trimethylene ring, the author has investigated the action of alkalis on the two substances described by him (this vol., 64) as trimethylenecarboxylic (ethyleneacetic) acid and benzoyltrimethylenecarboxylic (ethylenebenzoylactic) acid. If these acids were vinyl- and not trimethylene-derivatives they would readily be split up by alkalis into ketones and acids like the homo-



logous allyl derivatives. This is, however, not the case, as they may be boiled for hours with very concentrated potash without undergoing decomposition. The author therefore believes the acid obtained by Fittig and Roeder, and by himself, to be a trimethylene- and not a vinyl-derivative. He believes that in the formation of the hydrobromic acid compound a rupture of the ring takes place. This view is also strengthened by the researches of Freund on free trimethylene, Freund finding that hydriodic acts on trimethylene much more readily than bromine does.

L. T. T.

**Hydroxymaleic Acid.** By E. SCHERKS (*Ber.*, **17**, 698—699).—Bourgoin having described a hydroxymaleic acid prepared by shaking potassium bromomaleate with moist silver oxide (*Abstr.*, 1883, 1021), the author endeavoured to repeat his experiments, but although many modifications of the process were tried, they were invariably unsuccessful. The existence of this acid therefore would seem to be doubtful.

A. J. G.

**Action of Hydroxylamine on Chelidonic Acid and Meconic Acid.** By V. MEYER (*Ber.*, 1061—1062).—Hydroxylamine and its hydrochloride have no reaction on chelidonic acid. It is therefore unlikely that this acid is a ketone acid. Hydroxylamine, however, combines readily with meconic acid, forming an acid containing 1 atom of nitrogen. On this ground meconic acid will probably be found to be a ketone- or aldehyde-acid. The further investigation of this reaction and also of the action of hydroxylamine on comenic acid and hydrocomenic acid will be carried out by Odernheimer.

A. B.

**Pyrotritartaric Acid.** By C. BÖTTINGER (*Ber.*, **17**, 317—318).—When bromine is added to pyrotritartaric (uvic) acid suspended in water, the acid gradually dissolves, hydrobromic acid being formed at the same time. When sufficient bromine has been added, a very unstable yellow oil separates, whilst bromoform is deposited from the aqueous residue on neutralisation with sodium hydroxide. The yellow oil dissolves in cold sodium hydroxide with a yellow, in strong sulphuric acid with a dark cherry-red, coloration. In contact with water this oil decomposes, yielding hydrobromic acid, a dark resinous substance, and an oily brominated ketone, sparingly soluble in water, and volatile with steam. This ketone has a very penetrating odour, and dissolves in a solution of sodium carbonate, but the solution very soon undergoes decomposition. With hydrogen sodium sulphite, it forms an easily soluble crystalline substance. Heated with a solution of silver nitrate reduction takes place, and the smell of acetamide becomes perceptible; the resulting solution yields a reddish-brown silver salt on treatment with nitric acid. The author considers these results as confirmatory of the formula  $\text{CMe}:\text{C}.\text{CH}(\text{COOH}).\text{COMe}$ , proposed for pyrotritartaric acid by Baeyer and Perkin.

L. T. T.

**Conversion of Gluconic Acid into Normal Caprolactone.** By H. KILIANI and S. KLEEMANN (*Ber.*, **17**, 1296—1303).—Gluconic acid may be prepared by adding 2 parts of bromine to a cold solution

of 1 part of starch in 5 parts of water, and allowing it to remain for 30 to 36 hours. The liquid is then heated to drive off excess of bromine, and the hydrobromic acid is removed by adding the exact quantity of lead carbonate necessary to form lead bromide. The gluconic acid is then purified by means of its calcium salt.

1 part of the dried acid was mixed with 10 parts of concentrated hydriodic acid (b. p. 127°) and  $\frac{2}{3}$  parts amorphous phosphorus, and the whole digested for 7 hours, when the solution was found to contain caprolactone. This supports Fittig's formula for gluconic acid, at least as far as the normal character of the carbon-chain is concerned.

L. T. T.

**General Reaction for the Amido-fatty Acids.** By T. CURTIUS *Ber.*, 17, 959—960).—This reaction depends on the formation of a diazo-compound as previously described (this vol., p. 987). The substance to be tested is dissolved in absolute alcohol in a test-tube and treated with hydrochloric acid gas. The excess of hydrochloric acid and alcohol is then boiled off, the remaining liquid dissolved in a very small quantity of water, covered with ether, and a few drops of a concentrated solution of sodium nitrite added. Immediately a small quantity of nitrogen gas is evolved, as it is difficult to drive off all the hydrochloric acid. The liquid is agitated with the ether, and from the latter, on evaporation, the ethereal salt of the diazo-acid if present is obtained in oily drops. On adding hydrochloric acid, these give off quantities of nitrogen gas and become colourless. The altered and intense odour of a chlorinated ethereal salt may also be observed.

A. B.

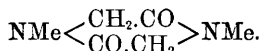
**Sarcosine.** By F. MYLIUS (*Ber.*, 17, 286—292).—In his original description of sarcosine, Liebig states that it sublimes unchanged if heated for some time at 100°. Strecker, in describing his synthetical sarcosine, says the crystals do not change in appearance at 100°, but melt at a slightly higher temperature and sublime unchanged. Believing the fused body to be no longer sarcosine, the author investigated the subject.

When sarcosine is heated in a retort, it appears to undergo no change below 200°; at 210° it begins to melt, and the fusion is complete at 220°. During fusion, water, carbonic acid, and dimethylamine are given off; the last two, however, in relatively small quantities. The fused mass in the retort forms a pale yellowish oil, which distils at about 350°, with scarcely any decomposition, and on cooling forms a white fibrous crystalline mass which yields colourless prisms when recrystallised from alcohol; these melt at 149—150°, are very easily soluble in water, and have a bitter taste and neutral reaction. Combustion showed its empirical formula to be  $C_3H_5NO$ , so that it had been formed according to the equation  $C_3H_7NO_2 = C_3H_5NO + H_2O$ . It is therefore *sarcosine anhydride*, but as will be seen from its compounds the empirical formula must be doubled, giving as its true formula  $C_6H_{10}N_2O_2$ . A vapour-density determination made according to Meyer's method, gave numbers approximating tolerably closely to those required by the formula  $C_6H_{10}N_2O_2$ , considering the decomposition which the substance undergoes above its boiling point. No salt

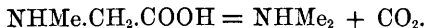
could be obtained by evaporating the anhydride with hydrochloric acid, but with a hydrochloric solution of platinic chloride a platino-chloride,  $2(\text{C}_6\text{H}_{10}\text{N}_2\text{O}_2), \text{H}_2\text{PtCl}_6 + 4\text{H}_2\text{O}$ , was formed, crystallising in hexagonal plates. Recrystallised from alcohol, it yields cubes or prisms with  $2\text{H}_2\text{O}$ . Sarcosine anhydride was obtained by Traube (*Abstr.*, 1883, 192), by passing cyanogen chloride through sarcosine in a melted state, but from analysis of the dehydrated platino-chloride, crystallised from alcohol, he assigned to it the formula  $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_3$ . With gold chloride, sarcosine anhydride yields an aurochloride,  $(\text{C}_6\text{H}_{10}\text{N}_2\text{O}_2)_2\text{HAuCl}_4 + 2\text{H}_2\text{O}$ , crystallising in glistening violet prisms. It also forms a double salt with mercuric chloride, which yields large colourless prisms. Treated in aqueous solution with bromine, transparent red crystals are formed, sparingly soluble in water; these are stable in an atmosphere of bromine, but on exposure to the air lose bromine and leave the unchanged anhydride. The anhydride is reconverted into sarcosine by heating it with aqueous hydrochloric or sulphuric acid, or by fusion with potash.

In aqueous solution, sarcosine anhydride is oxidised by a weak solution of potassium permanganate, with formation of dimethyl-oxamide and oxalic acid. Sarcosine, on the contrary, yields carbonic, nitrous, and nitric acids, and traces only of oxalic acid.

The author considers it probable that the constitution of sarcosine anhydride is represented by the formula



The secondary formation of dimethylamine and carbonic acid from sarcosine would be expressed by the equation



Kept for some time at a temperature slightly below its melting point, sarcosine yields a sublimate containing small quantities only of the unchanged substance.

L. T. T.

**Preparation of Carbamide.** By W. HENTSCHEL (*Ber.*, 17, 1286—1287).—A stream of dry ammonia is passed into phenyl carbonate heated on a water-bath, until the odour of ammonia becomes strongly marked. The product is then poured into hot water. On cooling, the liquid separates into a dark-coloured layer of phenol, and an aqueous solution of carbamide. 5 kilos. of the carbonate yield 1 kilo. carbamide, and almost the whole of the phenol is recovered. An almost theoretical yield of phenyl carbonate is obtained by passing dry phosgene gas into a solution of phenol in its equivalent quantity of dilute soda.

L. T. T.

**Alanine and Ethyl Oxalate: a Correction.** By H. SCHIFF (*Ber.*, 17, 1033—1034).—The substance which is described in a previous communication (*Ber.*, 17, 403) as ethylimidodiethyldioxamide has been found to contain a much smaller quantity of nitrogen than

that which by a clerical mistake it was supposed to contain and required theoretically. The investigation of this substance, which cannot be the above mentioned, will be continued. A. B.

**Uric Acid.** By E. FISCHER (*Ber.*, 17, 328—338).—Although phosphoric chloride fails to remove oxygen from uric acid, the author finds that if the uric acid is first methylated, two oxygen- and two hydrogen-atoms can be replaced by two chlorine-atoms, and that on further treatment a third chlorine-atom can be introduced in place of another oxygen- and another hydrogen-atom. These chlorines can then be replaced by hydrogen, ethoxyl, the amido-group, &c., thus giving a large number of derivatives. For convenience of nomenclature, the author looks upon all these as derivatives of a hypothetical non-oxygenised body,  $\text{CH}_3\text{C}_5\text{N}_4\text{H}_3$ , to which he gives the name *methylpurin*. Methyluric acid then becomes trihydroxymethylpurin, and so on. The methylated uric acid used in this research was prepared by heating neutral lead urate with 2 mols. of methyl iodide for 30 hours at  $100^\circ$ . The product probably consisted of a mixture of mono- and di-methyluric acid, but these were not separated.

*Dichlorhydroxymethylpurin*,  $\text{C}_5\text{N}_4\text{Me}(\text{OH})\text{Cl}_2$ , was obtained by heating 10 parts of the above described methylated uric acid with 13 parts phosphoric chloride and 50 parts phosphoric oxychloride for 8—9 hours at  $130^\circ$ . The oxychloride was distilled off, the residue decomposed with water, and the whole evaporated to dryness. The residue is extracted with water, when a dark-brown partly crystalline mass is left, which contains all the dichlorhydroxymethylpurin. This mass is then heated with strong nitric acid, when a violent action takes place, all the bye-products (which are to form the subject of another paper) being converted into easily soluble compounds. On the addition of water, dichlorhydroxymethylpurin is precipitated in an almost pure state. When recrystallised from alcohol, it forms thin white needles melting at  $274^\circ$ . It is more stable than uric acid, volatilises undecomposed, and is not attacked by boiling with fuming nitric acid or hydrochloric acid and potassium chlorate. It dissolves easily in alkalis, and can be boiled with them without decomposition. The chlorine-atoms are replaced by hydrogen by treatment with fuming hydriodic acid.

*Trichloromethylpurin*,  $\text{C}_5\text{N}_4\text{MeCl}_3$ , is obtained by heating 1 part of the dichloro-derivative with  $1\frac{1}{4}$  parts phosphoric chloride and 5 parts phosphoric oxychloride in closed tubes at  $160^\circ$  for 8 hours. It crystallises in small colourless needles which melt at  $174^\circ$ . It is insoluble in alkalis, and, unlike the dichloride, is easily reconverted into methyluric acid. When heated on the water-bath with alcoholic soda, it yields diethoxychloromethylpurin, which crystallises in needles; but if the action of the alkali be continued, a substance is produced which is free from chlorine, melts under boiling water, and is probably triethoxymethylpurin. If diethoxychloromethylpurin is heated with fuming hydrochloric acid at  $130^\circ$ , it is converted into  $\text{C}_5\text{N}_4\text{MeH}_3\text{O}_3$ , which, from its reactions, &c., is undoubtedly a mono-methyluric acid. This body is almost as sparingly soluble as uric acid, requiring for solution more than 2000 parts of boiling water, and

therefore appears to be different from the methyluric acid described by Hill (this Journal, 30, 75).

*Hydroxymethylpurin*,  $C_5N_4MeH_3O$ , obtained by the reduction of dichloroxymethylpurin by fuming hydriodic acid, crystallises in colourless prisms, melting at  $233^\circ$ , and easily soluble in water to an alkaline solution. Its hydriodide crystallises in colourless scales, soluble in alcohol and water; the hydrochloride is easily soluble in water, sparingly so in alcohol. The aurochloride crystallises in thin yellow plates; the platinochloride in orange prisms. In slightly acid solutions, silver nitrate precipitates silver hydroxymethylpurin as a white crystalline powder. As hydroxymethylpurin has the composition of a methylsarcine, the author endeavoured to methylate sarcine by acting on its di-silver derivative with methyl iodide. He obtained a dimethylsarcine, which, however, differed from hydroxymethylpurin and also from hydroxydimethylpurin.

*Dichloroxydimethylpurin*,  $C_5N_4Me_2OCl_2$ , is obtained by acting on the lead salt of the monomethyl-derivative with methyl iodide. It crystallises in thin, slightly coloured needles, which melt at  $183^\circ$ . It is insoluble in alkalis, but is decomposed by boiling alkalis. Alcoholic potash removes one chlorine-atom at ordinary temperatures, the second on heating, ethoxyl being introduced in their place.

*Hydroxydimethylpurin*,  $C_5N_4Me_2H_2O$ , is easily obtained from the dichloro-derivative by reduction with hydriodic acid. It crystallises in needles melting at  $112^\circ$ . It is easily soluble in alcohol and water to a strongly alkaline solution; sparingly soluble in ether, almost insoluble in alkalis. Its aurochloride gives characteristic yellow needles. It has the composition of dimethylsarcine, but is not identical with that above described; and the author is at present in doubt whether it should be regarded as a dimethylsarcine or not.

*Ethoxychloroxydimethylpurin*,  $C_5N_4Me_2OCl.OEt$ , is obtained by acting on dichloroxydimethylpurin with 50 per cent. alcoholic potash, the temperature not being allowed to rise above  $40^\circ$ . It often crystallises in a mass of slender needles, but gradually changes into heavier crystalline agglomerations which fuse at  $160^\circ$ . When heated with fuming hydriodic acid, it loses chlorine and ethoxyl and yields trihydroxydimethylpurin.

*Dihydroxydimethylpurin*,  $C_5N_4Me_2H_2O_2$ , is formed by heating ethoxychloroxydimethylpurin with ten times its weight of fuming hydriodic acid. This substance is crystalline and distils unchanged. Although identical with theobromine in composition, it differs from it in properties, but shows its relation to uric acid by giving the murexide reaction.

*Diethoxyoxydimethylpurin*,  $C_5N_4Me_2O(OEt)_2$ , prepared from the dichloro-derivative by boiling it with excess of alcoholic soda, crystallises from water in minute scales melting at  $126-127^\circ$ . It is easily soluble in alcohol, sparingly so in water. It is insoluble in alkalis, but easily soluble in concentrated hydrochloric acid. If heated with strong hydrochloric acid, in sealed tubes at  $130^\circ$ , it loses both ethyl-groups, and is converted into *trihydroxydimethylpurin*. The reaction is more rapid with concentrated sulphuric acid at a temperature of  $140^\circ$ .

*Trihydroxydimethylpurin*,  $C_5N_4Me_2H_3O_3$ , forms almost colourless crystals which melt at a very high temperature, undergoing decomposition at the same time. It is sparingly soluble in boiling water. This body is not decomposed by boiling with ammoniacal silver nitrate, but yields a gelatinous silver salt on evaporation of the excess of ammonia, thus differing entirely from the dimethyluric acid described by Hill. Chlorine or potassium chlorate and hydrochloric acid decompose it quickly into easily soluble products, but only very slight traces of any compound resembling alloxan. The principal product is an easily soluble crystalline substance which the author is now investigating. The author postpones any discussion of the uric acid formula until his researches are further advanced.

L. T. T.

**Chemical Nomenclature.** By A. BAEYER (*Ber.*, 17, 960—963).—In this paper, the author describes a method of naming complicated organic substances by which from the name alone the exact position of the atoms and groups of atoms may at once be understood. Organic bodies may be divided into three classes; 1st, those in which there is an open chain of carbon-atoms; 2nd, those in which the chain is closed; and, 3rd, those in which there are both open and closed chains. The position of the atoms in the first is usually shown by means of Greek letters, and in the second by the use of Arabic numbers. In cases such as naphthalene and quinoline when there are two rings of atoms, one ring is represented by numbers and the other by letters. The author proposes to use letters for these rings. Thus using for the benzene-ring the letter B, and for the pyridine-ring the letters Py; the constitutional formula corresponding to the name B 1·4-dichloro-, Py 1·3-dihydroxy-quinoline, is readily understood to be that of a quinoline in which two particular hydrogen-atoms in the benzene-ring have been replaced by chlorine-atoms, and two particular hydrogen-atoms in the pyridine-ring by hydroxyls, provided the order in which the atoms are to be counted is fixed. In naphthalene the letters B and BB', and in anthracene -B, -BB', and perhaps A for the middle ring, may be used; thus, for example, phenylanthracene is a name which may have a treble meaning, and distinction has to be drawn between A phenylanthracene, B phenylanthracene, and BB' phenylanthracene.

In the case of open chains, the present system of naming by means of Greek letters may be used with a slight alteration. There is an inconvenience in the present system that in substituted acids the first carbon-atom, that of the carboxyl-group, is not named  $\alpha$  but the one next to it, whilst in substituted hydrocarbons the first carbon-atom is named  $\alpha$ . The author now proposes in all cases to call the first carbon-atom by the last letter of the Greek alphabet,  $\omega$ , and the carbon-atoms next to it in order  $\alpha$ ,  $\beta$ ,  $\gamma$ , &c. The nomenclature of acids remains unaltered, but it is altered in substituted hydrocarbons;  $\alpha$ -chlorostyrolene,  $Ph.CH:CHCl$ , becomes  $\omega$ -chlorostyrolene, and  $\beta$ -chlorostyrolene,  $Ph.CCl:CH_2$ , becomes  $\alpha$ -chlorostyrolene. There are scarcely any other similar changes, and the drawback in this case might be diminished by styling the present  $\beta$ -chlorostyrolene,  $\alpha$ -\*chlorostyrolene.

The following are examples of this change in nomenclature :—

Benzyl chloride .....	= <i>ω</i> -chlorotoluene,
Benzylene dichloride .....	= <i>ω</i> -dichlorotoluene,
Benzenyl trichloride .....	= <i>ω</i> -trichlorotoluene,
<i>o</i> -Xylylene bromide .....	= <i>ω</i> <sub>2</sub> -dibromo- <i>o</i> -xylene,
Mesitylene with 3 Cl in 3 methyls	= <i>ω</i> <sub>3</sub> -trichloromesitylene,
Mesitylene with 3 Cl in 1 methyl	= <i>ω</i> -trichloromesitylene,
Ph.CH <sub>2</sub> .CH <sub>2</sub> Br .....	= <i>ω</i> -bromomethylbenzene,
Ph.CHBr.CH <sub>3</sub> .....	= <i>α</i> -bromomethylbenzene,
<i>α</i> -Chlorostyrolene .....	= <i>ω</i> -chlorostyrolene,
<i>β</i> -Chlorostyrolene .....	= <i>α</i> -chlorostyrolene,
Acetophenone bromide .....	= <i>ω</i> -bromacetophenone,
Ph.CH <sub>2</sub> .CH <sub>2</sub> .CH <sub>2</sub> Br .....	= <i>ω</i> -bromopropylbenzene,
Ph.CH <sub>2</sub> .CHBr.CH <sub>3</sub> .....	= <i>α</i> -bromopropylbenzene,
Ph.CHBr.CH <sub>2</sub> .CH <sub>3</sub> .....	= <i>β</i> -bromopropylbenzene.

For a compound in which substitution takes place both in the closed ring and in the side chain, the above signs require to be combined. Thus an acetophenone bromide in which the benzene-ring is also brominated in the para-position, is *ω*-bromo-4-brom-acetophenone, or more shortly *ω*-4-dibromacetophenone. A substituted cinnamic acid in which one hydrogen-atom is replaced in the ring, or one in the side chain by bromine, may be called *α*-4-dibromo-cinnamic acid. A quinaldine, in which hydrogen in the methyl-group, in the pyridine-ring, and in the benzene-ring, has been replaced by hydroxyl groups, may be named *ω*-Py2-B1-trihydroxyquinaldine.

The author also proposes to use the prefixes *eso-* or *es-*, and *exo-* or *ex-* to express compounds in which hydrogen-atoms are substituted, either in the closed ring or open chain, but the more exact position of which is not known or expressed. For example, three dichlorethylbenzenes are possible in which the hydrogen-atoms in each case are substituted in the side chain. When the exact position is unknown they may be called exodichlorethylbenzene. If three hydrogen-atoms are also substituted in the benzene-ring, it may be esotrichloro-exodichlorethylbenzene. Again, if the total number of chlorine-atoms are known, but the exact positions are unknown, it may be called *eso-exo-pentachlorethylbenzene*. Lastly, in a similar way, if the position of the substituted atoms is only known in part of the compound, this method is of use. For example, in the case of a quinoline-cinnamic acid in which in the benzene-ring, in the pyridine-ring, and in the side chain, hydrogen-atoms have been replaced by hydroxyl-groups, but the exact position of these is unknown, the name and constitution of the acid may be expressed as B-hydroxy-Py-hydroxy-ex-hydroxyquinolinecinnamic acid, or more shortly as B-Py-exotrihydroxyquinolinecinnamic acid; and if it is uncertain in which part of the quinoline the substitution has taken place, as *es-dihydroxy-ex-hydroxyquinolinecinnamic acid*.

N.B.—This system of nomenclature is used by Baeyer and his collaborators in their recently published communications.

A. B.

**Xylenes.** By A. COLSON (*Compt. rend.*, **98**, 1543—1545).—*Orthoxylylene glycol* (*phthalic glycol*),  $C_6H_4(CH_2.OH)_2$ , is obtained by boiling orthodibromo-xylene with the requisite quantity of potassium carbonate, and 20 or 30 times its weight of water, filtering, evaporating to dryness in a vacuum, and extracting the residue with ether. It forms rhomboidal plates, which melt at  $64.5^\circ$ , and readily remain in superfusion; sp. gr. of the liquid at  $75^\circ = 1.141$ . The glycol has a bitter taste, and dissolves in five times its weight of ether and six times its weight of water, but is more soluble in alcohol. When boiled with concentrated hydrochloric or hydrobromic acid, it yields the corresponding chloride or bromide.

*Orthodibromo-xylene* is obtained by adding bromine drop by drop to orthoxylylene heated at  $140$ — $190^\circ$ . The liquid is filtered and the solid product washed with ether and purified by repeated crystallisation from alcohol. It melts at  $94.6^\circ$ , and is more soluble in hot ether, alcohol, and light petroleum than in these liquids when cold. On oxidation, it yields phthalic acid, and it is partially saponified by alcohol.

*Orthodichloro-xylene*, obtained by the action of concentrated hydrochloric acid on the glycol, is a crystalline substance which melts at  $54.8^\circ$ , and sublimes easily; sp. gr. at  $20^\circ = 1.33$ . It is very soluble in ether and light petroleum. The dichloro-xylene obtained by Rayman (*Bull. Soc. Chim.*, **26**, 532), melting at  $103^\circ$ , was doubtless 1 : 4 dichloro-xylene.

C. H. B.

**Tribenzoylmesitylene.** By E. LOUISE (*Compt. rend.*, **98**, 1440—1442).—Monobenzoyl- or dibenzoyl-mesitylene is dissolved in an excess of benzoic chloride, and heated with aluminium chloride at  $198^\circ$ , the product washed with water, and the black residue extracted with boiling alcohol. As the alcoholic solution cools, it deposits amber-coloured crystals of symmetrical tribenzoyl-mesitylene,  $C_{30}H_{24}O_3$ . This compound melts at  $215$ — $216^\circ$ , is almost insoluble in cold alcohol, more soluble in boiling alcohol, ether, benzene, &c., but most readily dissolved by a mixture of chloroform and acetone. From this latter solvent it is deposited in large oblique rhombic prisms, the acute angle of which  $= 76^\circ 46'$ , and the angle of the principal face on the lateral face,  $P : m = 94^\circ 10'$ .

The formation of the benzoyl-derivatives of mesitylene is a function of the temperature. Below  $118^\circ$  the mono-derivative is formed alone, the di-derivative at  $150^\circ$ , and the tri-derivative at  $198^\circ$ .

C. H. B.

**Phenethyl Compounds.** By K. MAINZER (*Ber.*, **17**, 1160).—A question of priority.

**Condensation Products of Thiophene with Aldehydes, Methylal, and Benzyl Alcohol.** By A. PETER (*Ber.*, **17**, 1341—1347).—Corney (*Ber.*, **17**, 790) has shown that the Friedel-Crafts reaction is applicable to thiophene, and Nahnsen (*Ber.*, **17**, 789) that dithienyl, analogous to diphenyl, is formed by passing thiophene through tubes heated to dull redness. The author has further investigated the analogy between benzene and thiophene.



*Dithienyltrichlorethane*,  $\text{CCl}_3\cdot\text{CH}(\text{C}_4\text{H}_3\text{S})_2$ , analogous to the diphenyltrichlorethane obtained by Baeyer, is prepared as follows:—10 grams of chloral and 23 grams of crude thiophene (about half thiophene, half benzene) is dissolved in 200 glacial acetic acid; to this solution an equal volume of a mixture of equal parts of glacial acetic and strong sulphuric acids is gradually added, and finally concentrated sulphuric acid until the mixture no longer gives the thiophene reaction. The product is then poured into cold water, and purified in the usual way. Dithienyltrichlorethane is easily soluble in ether, carbon bisulphide, and boiling alcohol, sparingly in cold alcohol. It melts at  $76^\circ$ , and gives a very intense violet-red coloration when heated with sulphuric acid and isatin; so that mere traces can be detected by this reaction. The yield of dithienyltrichlorethane is about 30 per cent., but the aqueous filtrate contains a considerable quantity of its sulphonic acid.

*Dithienyldichlorethylene*,  $\text{CCl}_2:\text{C}(\text{C}_4\text{H}_3\text{S})_2$ , was obtained from the trichloro-compound by treatment with  $1\frac{1}{4}$  mols. potassium hydroxide, but a better yield was obtained when the latter was replaced by potassium cyanide. It forms a colourless oil, which distils in a current of steam, and gives a violet-blue colour with sulphuric acid and isatin in the cold. Unlike the trichloro-derivative, it is decomposed by sulphuric acid.

*Hexabromodithienyltrichlorethane*,  $\text{CCl}_3\cdot\text{CH}(\text{C}_4\text{Br}_3\text{S})_2$ , was obtained by brominating the trichloro-derivative. It forms a white crystalline powder, soluble in boiling alcohol. It gives no colour reaction with sulphuric acid and isatin.

*Dithienyltribromomethane*,  $\text{CBr}_3\cdot\text{CH}(\text{C}_4\text{H}_3\text{S})_2$ , obtained from bromal and thiophene, crystallises in small well-formed pyramids, which melt at  $101\text{--}102^\circ$ ; and is analogous in its properties to the dithienyltrichlorethane.

*Dithienyldibromomethylene* is obtained by the action of potassium hydroxide or cyanide on the tribromo-compound. It is a colourless oil, which can be distilled with steam; and resembles the dichloro-derivative in properties.

*Dithienylmethane*,  $\text{CH}_2(\text{C}_4\text{H}_3\text{S})_2$ , was obtained by Baeyer's reaction for obtaining diphenylmethane. The yield, however, never exceeded 10 per cent., as a great deal of decomposition and formation of the sulphonic acid took place. It is a colourless oil, having an odour of oranges, and boiling at  $267^\circ$ . With isatin and sulphuric acid it gives a red coloration in the cold, but the colour becomes more intensely warming the mixture. Sulphuric acid alone causes decomposition. In one preparation of dithienylmethane, the oil solidified to lanceolate crystals; these melted at  $43^\circ$ , and showed the characteristic reaction of dithienylmethane with isatin and sulphuric acid, but they only weighed 0.03 gram, and the author has not been able to obtain the oil again in a crystalline state.

*Phenylthienylmethane*,  $\text{CH}_2\text{Ph}(\text{C}_4\text{H}_3\text{S})$ , was obtained by digesting benzyl alcohol and thiophene with stannic chloride. A better yield was obtained, however, by dissolving 5 grams of benzyl alcohol, and 6 grams of pure thiophene which was diluted with its own volume of light petroleum, in 100 grams glacial acetic acid; then adding an

equal volume of a mixture of equal parts of sulphuric and glacial acetic acids, and then sulphuric acid until the thiophene reaction could no longer be obtained. Phenylthienylmethane is an oil of fruity odour, and boils at  $265^{\circ}$  (uncorr.). With sulphuric acid and isatin in the cold, it gives a red coloration, which turns to a magenta-red on warming. It does not decompose so readily with sulphuric acid as most of the foregoing compounds.

L. T. T.

**Preparation of Phenyl Cyanate.** By W. HENTSCHEL (*Ber.*, **17**, 1284—1285).—If a stream of phosgene gas be passed over fused carbanilide, phenyl cyanate distils over as a colourless oil. A still easier method of obtaining it consists in melting dry aniline hydrochloride in a retort, and passing over it a current of phosgene gas: hydrochloric acid is given off, and phenyl cyanate distils over. The phenyl cyanate absorbs a good deal of hydrochloric acid, and becomes solid, but on redistillation gives up the acid, and then remains liquid. It would seem, therefore, to possess slightly basic properties, and to form a compound with hydrochloric acid, similar to that formed by cyanic acid. These methods render it very easy to prepare phenyl cyanate in quantity.

L. T. T.

**Ethylphenol.** By H. AUER (*Ber.*, **17**, 669—673).—Propyl-, butyl-, and amyl-phenols have been prepared by Liebmann (*Abstr.*, 1882, 171, 727) by condensation from the respective fatty alcohols and phenol by aid of zinc chloride; and methylpropylphenol has been prepared by Mazzara (*Abstr.*, 1883, 463), using, however, magnesium chloride as the dehydrating agent. The author has applied this reaction to the preparation of ethylphenol.

Equivalent quantities of phenol and absolute alcohol, with about twice the weight of zinc chloride, were heated in a vessel provided with a reflux condenser. The temperature remained for a long time constant at  $173^{\circ}$ , then slowly rose to  $181^{\circ}$ , when the reaction was stopped. The main products of the reaction were ethylphenol and ethylphenetoil; they can be separated by treatment with dilute aqueous potash, in which the former alone is soluble. *Ethylphenol*,  $C_6H_4Et.OH$ , so obtained forms an oily colourless liquid, boils between  $191^{\circ}$ — $215^{\circ}$ , has sp. gr. 1.049 at  $14^{\circ}$ , is sparingly soluble in water, readily soluble in ether and alcohol. With ferric chloride, it gives a dirty green coloration. It is probably identical with the  $\beta$ -ethylphenol obtained by Beilstein and Kuhlberg by the action of potash on  $\beta$ -ethylbenzenesulphonic acid. *Ethylphenetoil*,  $C_6H_4Et.OEt$ , is a mobile colourless liquid of strong, persistent, aromatic odour. It turns yellow on exposure to light. It is insoluble in water, soluble in alcohol and ether. Sp. gr. = 0.986 at  $14^{\circ}$ . *Ethylphenolphthaleïn*,  $C_{22}H_{18}O_4 + H_2O$ , prepared by heating ethylphenol with phthalic acid and zinc chloride, forms a pale reddish-grey crystalline powder, insoluble in water, readily soluble in ether and alcohol. It closely resembles phenolphthaleïn, but is distinguished from it by its alkaline solution having a violet-red colour, by not being decomposed below  $139^{\circ}$ , and by the greater instability of its compound with ammonia.

Methyl alcohol, when heated with phenol and zinc chloride, yields only anisöl, and that in very small quantity. A. J. G.

**High-boiling Phenols contained in Coal-tar.** By E. NÖLTING (*Ber.*, **17**, 386—387).—The coal-tar oils boiling above 300° probably contain the phenols of anthracene and phenanthrene.

W. C. W.

**Ethereal Salts of Nitrosophenol.** By J. F. WALKER (*Ber.*, **17**, 399—401).—Sodium nitrosophenol is best prepared by adding phenol (1 mol.) to a concentrated alcoholic solution of sodium ethylate (1 mol.), and stirring the mixture thoroughly with amyl nitrite (1 mol.). The solution is then evaporated over sulphuric acid, and the residue is washed with ether and dried on porous tiles. *Benzoyl-nitrosophenol*,  $C_6H_4(NO).O\bar{B}z$ , obtained by adding benzoic chloride to sodium nitrosophenol covered with a layer of anhydrous chloroform or ether, is a yellow crystalline substance which melts at 168° with decomposition. It dissolves freely in chloroform and in hot alcohol. It is decomposed by boiling with alkalis. *Ethyl nitrosophenol-carboxylate*,  $C_6H_4(NO)O.CO\bar{O}Et$ , crystallises in golden needles, which melt at 109°. It is soluble in chloroform and in hot alcohol. The corresponding methyl compound forms yellow prisms which melt at 137°. Mononitrosoresorcinol yields analogous compounds.

W. C. W.

**Nitroso-orthocresol.** By E. NÖLTING and O. KOHN (*Ber.*, **17**, 370—371).—Nitroso-orthocresol is prepared by slowly adding nitrosyl sulphate to orthocresol dissolved in 30 times its weight of water. After purifying the product by Ter Meer's process (*Ber.*, **8**, 623), the nitrocresol is obtained in white needles, soluble in alcohol, ether, chloroform, or hot water. The crystals melt at 135°, with decomposition. The sodium salt is deposited from acetone in brown needles containing 3 mols.  $H_2O$ . The potassium salt is anhydrous. Both salts dissolve freely in alcohol and in water. The aqueous solution yields precipitates with the salts of the heavy metals.

On oxidation by potassium ferricyanide, nitrosocresol is converted into the nitroorthocresol, melting at 95°, described by Neville and Winther (*Ber.*, **15**, 2978). Nitric acid (sp. gr. 1.33) converts it into dinitroorthocresol, melting at 86°. On reduction, the nitroso-compound yields the amidocresol, melting at 175°, which is also obtained by the reduction of the azo-compounds of orthocresol (see this vol., p. 902). The nitroso-group in this compound stands in the para-position as regards the hydroxyl.

W. C. W.

**Two Isomeric Phenyl Methyl Glycols.** By T. ZINCKE (*Ber.*, **17**, 708—713).—Some time back the author showed that two alcohols might be obtained from stilbene bromide or chloride—hydrobenzoïn and isohydrobenzoïn—both of which can only be expressed by the same formula,  $CHPh.(OH).CHPh.OH$  (*Abstr.*, 1877 [i], 460). Later, in conjunction with Wachendorff and Breuer (*Abstr.*, 1878, 885), he found that styrolene bromide,  $CHPhBr.CH_2Br$ , yields only a single

dihydric alcohol. In his present communication, he extends his researches to the dibromide  $\text{CHPhBr} \cdot \text{CHMeBr}$ , obtained by the bromination of propylbenzene, and finds that this also yields two isomeric phenyl methyl glycols,  $\text{CHPh(OH)CHMe.OH}$ .

$\alpha$ -Phenyl methyl glycol is prepared by boiling the dibromide in acetic acid solution with potassium acetate, diluting with water, extracting the acetate formed with ether, and saponifying with alcoholic potash. It forms large tabular crystals which melt at  $52-53^\circ$ . It is readily soluble in water, alcohol, ether, acetone, benzene, and chloroform, sparingly soluble in light petroleum.

$\beta$ -Phenyl methyl glycol is prepared by converting the dibromide into the benzoate and saponifying, or by boiling the dibromide for three to four days with a solution of potassium carbonate (1:6). It is crystalline, melts at  $92-93^\circ$ , and is markedly less soluble than the  $\alpha$ -alcohol in the solvents mentioned above. The investigation of these bodies and some related compounds is in progress.

A. J. G.

**Trinitro-resorcinol.** By E. NÖLTING and A. COLLIN (*Ber.*, **17**, 259—261).—When styphnic ether is heated with a solution of sodium hydroxide or carbonate, sodium styphnate is formed. If a cold alcoholic solution of the ether is mixed with excess of alcoholic ammonia, and the whole allowed to stand, the liquid becomes red, then yellow, and deposits the trinitrometaphenylenediamine,  $\text{C}_6\text{H}(\text{NH}_2)_2(\text{NO}_2)_3$  [ $\text{NH}_2 : \text{NO}_2 : \text{NH}_2 : \text{NO}_2 = 1 : 2 : 3 : 4 : 6$ ] in the form of yellow microscopic needles. This substance is very sparingly soluble in the ordinary solvents, and melts at a very high temperature. Ammonia is evolved on heating it with dilute soda, and sodium styphnate is re-formed. No trace of nitrous acid could be detected by Griess' reaction in the mother-liquors from which the trinitrophenylenediamine had crystallised. Styphnic acid (trinitroresorcinol), when heated with aniline, yields an aniline salt, but no trace of diazoamidobenzene. Styphnic ether and aniline yield a crystalline body, probably  $\text{C}_6\text{H}(\text{NO}_2)_3(\text{NHPh})_2$ , but not further investigated; no trace of diazoamidobenzene was found. From these reactions, the authors consider that the positions of the side groups in styphnic acid must be [ $\text{OH} : \text{NO}_2 : \text{OH} : \text{NO}_2 = 1 : 2 : 3 : 4 : 6$ ]. If either of the other two possible formulæ [ $1 : 2 : 3 : 4 : 5$ , or  $1 : 3 : 4 : 5 : 6$ ] were correct, nitrous acid should be eliminated when styphnic acid is treated with alkalis or ammonia. (Compare also Henriques, *Abstr.*, 1883, 327.)

L. T. T.

**Nitrobenzyl Chlorides and Iodides.** By G. KUMPF (*Ber.*, **17**, 1073—1074).—On nitrating benzyl chloride, besides solid paranitrobenzyl chloride, an oily mother-liquor is left from which, after a time, two kinds of crystals are deposited. Some of these are needles having the form of paranitrobenzyl chloride, but others have quite a different form, being thick and rhombic. The author carefully picked out the latter, and found them to be a nitrobenzyl chloride giving, on oxidation, orthonitrobenzoic acid of melting point  $147^\circ$ ; they are therefore crystals of orthonitrobenzyl chloride.

On boiling orthonitrobenzyl chloride with potassium iodide and alcohol, orthonitrobenzyl iodide is formed. It crystallises in rhombic plates, and melts at  $75^{\circ}$ . Paranitrobenzyl iodide prepared in the same way from paranitrobenzyl chloride crystallises in colourless needles, and melts at  $127^{\circ}$ . A. B.

**Orthonitrobenzyl Chloride.** By E. NÖLTING (*Ber.*, **17**, 385—386).—The oil which is obtained as a bye-product in the preparation of paranitrobenzyl chloride (which is crystalline) is oxidised by potassium permanganate, yielding orthonitrobenzoic acid. It consists chiefly of orthonitrobenzyl chloride. W. C. W.

**Paranitrophenyl-benzyl Ethers and Phenyl Paranitrobenzyl Ethers.** By G. KUMPF (*Ber.*, **17**, 1075—1078).—A number of nitro-derivatives of phenyl benzyl ether have been prepared. The general method has been to act on benzyl chloride or paranitrobenzyl chloride with the potassium salt of nitrophenol. As the potassium salts of dinitrophenol and picric acid have no action on benzyl chloride, the silver salts and benzyl iodide were used. The ethers obtained are as a rule crystalline, and soluble in benzene or glacial acetic acid. The following were prepared:—Paranitrophenyl benzyl ether,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\text{Ph}$ , melting at  $106^{\circ}$ ; orthonitrophenyl benzyl ether, melting at  $29^{\circ}$ ;  $\alpha$ -dinitrophenyl benzyl ether ( $\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{O}\cdot\text{CH}_2\text{Ph}$ , melting at  $149^{\circ}$ ;  $\beta$ -dinitrophenyl benzyl ether, melting at  $76^{\circ}$ ; benzyl picrate,  $(\text{NO}_2)_3\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\text{Ph}$ , melting at  $149^{\circ}$ ; phenyl paranitrobenzyl ether,  $\text{PhO}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , melting at  $91^{\circ}$ ; paranitrophenyl paranitrobenzyl ether,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , melting at  $183^{\circ}$ ; orthonitrophenyl paranitrobenzyl ether, melting at  $129^{\circ}$ ;  $\alpha$ -dinitrophenyl paranitrobenzyl ether,  $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{O}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , melting at  $201^{\circ}$ ;  $\beta$ -dinitrophenyl paranitrobenzyl ether, melting at  $137^{\circ}$ ; paranitrobenzyl picrate,  $(\text{NO}_2)_3\text{C}_6\text{H}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , melting at  $108^{\circ}$ . A. B.

**Ethyl Phenylcarbonate.** By B. PAWLEWSKI (*Ber.*, **17**, 1205).—When aluminium chloride is added in successive portions to a mixture of phenol and ethyl chlorocarbonate, ethyl phenylcarbonate is formed. This compound has been described by Fatianow (*Jahresb.*, 1864, 447). W. C. W.

**Aniline Derivatives.** By A. CLAUS and H. HOWITZ (*Ber.*, **17**, 1324—1328).—With the idea of throwing light on the valency relationships of atoms, the authors have examined the di-substituted anilines and tetra-substituted ammonium iodides.

*Methylethylaniline*,  $\text{NPhMeEt}$ , was prepared by methylating ethylaniline, by ethylating methylaniline, and finally by decomposing the methiodide of diethylaniline with alcoholic potash. The substance obtained was in all cases identical. It is a colourless oil, which boils at  $201^{\circ}$  (uncorr.) It combines very readily, even in the cold, with methyl iodide to form *dimethylethylphenylammonium iodide*, which melts at  $126^{\circ}$ , is identical with dimethylaniline ethiodide, previously described by Claus and Rautenberg, and to which the

erroneous melting point  $124.5^{\circ}$  was then ascribed. Treated with alcoholic potash, this quaternary iodide yields dimethylaniline, boiling at  $192^{\circ}$ , the identity of which was further proved by bromination, when dimethylparabromophenylamine, melting at  $55^{\circ}$ , was formed. *Diethylaniline methiodide*, mentioned above, was obtained by digesting molecular proportions of diethylaniline and methyl iodide for some time on the water-bath. It melts at  $102^{\circ}$ , and is identical with the ethiodide of methylethylaniline. These results prove that, at least as far as ethyl and methyl are concerned, the order of the introduction of the single radicals in ammonium compounds has no influence on the final compound obtained, and that by the decomposition of the tetra-substituted ammonium iodides by alcoholic potash, that alcohol radical is split off which contains most carbon-atoms. The authors now intend to carry on their investigations with analogous compounds containing propyl, butyl, &c.

*Diethylbromophenylamine*,  $\text{NEt}_2\cdot\text{C}_6\text{H}_4\text{Br}$ , crystallises in colourless needles or prisms, which melt at  $33^{\circ}$ , and boil at  $270^{\circ}$ .

*Methylethylbromophenylamine* is a colourless oil, which boils at  $265^{\circ}$ , and solidifies below  $0^{\circ}$  to easily fusible needles.

*Dimethylpropylphenylamine*,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\text{Pr}$ , was prepared by treating an ethereal solution of dimethylparabromophenylamine with propyl bromide and sodium. It is a colourless oil, boiling at  $230^{\circ}$  (uncorr.). It combines readily with methyl iodide, even in the cold, forming trimethylpropylphenylammonium iodide, which crystallises in colourless needles, melting at  $168^{\circ}$ . Treatment with alcoholic potash reproduces dimethylpropylphenylamine. L. T. T.

**Action of Aniline on Pyrotartaric Acid.** By C. BÖTTINGER (*Ber.*, 17, 996—999).—On heating a mixture of aniline and pyrotartaric acid, a violent reaction takes place, and carbonic acid and water are given off. From the liquid thus obtained, a yellowish-white precipitate is thrown down by hydrochloric acid, which, after being washed with water, may be crystallised in fine needles from alcohol. Only a very small quantity, however, crystallises, and on evaporating the mother-liquor a thick mass is obtained, from which only a very little of the crystalline substance can be extracted. The crystalline substance melts at  $194.5^{\circ}$ , and distils undecomposed when heated in small quantities at a time. It is soluble in alcohol, ether, chloroform, and benzene. It dissolves in concentrated hydrochloric acid, and from this solution double salts of mercuric chloride and platonic chloride are obtained. When heated with alcohol and concentrated hydrochloric acid at  $150^{\circ}$  in a closed tube, some aniline or ethylaniline is formed. Analysis leads to the formula  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}$ , and it is possibly a hydroxy-derivative of ethylidenediphenylamine. Lazarus, who has prepared this substance, has also obtained a compound of the formula  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}$  by the action of paratoluidine on pyrotartaric acid.

A. B.

**Nitro-orthotoluidine of Melting Point  $107^{\circ}$  and its Derivatives.** By E. NÖLTING and A. COLLIN (*Ber.*, 17, 268—272).—When the *nitro-orthotoluidine* obtained by the authors (see p. 1012) by

nitrating orthotoluidine dissolved in 10 parts of concentrated sulphuric acid, is reduced with tin and hydrochloric acid, it yields metatoluylenediamine,  $\text{C}_6\text{H}_3\text{Me}(\text{NH}_2)_2$  [ $\text{NH}_2 : \text{Me} : \text{NH}_2 = 1 : 2 : 5$ ], and therefore has the constitution  $\text{C}_6\text{H}_3\text{Me}(\text{NH}_2)(\text{NO}_2)$  [ $\text{NH}_2 : \text{Me} : \text{NO}_2 = 1 : 2 : 5$ ]. It crystallises in well-formed bright yellow monosymmetric prisms, melting at  $107^\circ$ , and is soluble in ether, alcohol, and acetone, sparingly so in water. The *sulphate* crystallises in yellow scales, which are slowly decomposed by water; the *nitrate* also forms yellow scales. By boiling it with  $1\frac{1}{2}$  times its weight of acetic anhydride an *acetoneitrotoluide* is obtained, crystallising in yellowish-white needles, melting at  $150\text{--}151^\circ$ .

Nitro-orthocresol,  $\text{C}_6\text{H}_3(\text{OH})\text{Me}(\text{NO}_2)$  [ $\text{OH} : \text{Me} : \text{NO}_2 = 1 : 2 : 5$ ], obtained from the nitrotoluide by means of the diazo-reaction, crystallises from boiling light petroleum in long pliant yellow needles, melting at  $106\text{--}108^\circ$ . It is sparingly soluble in cold water, light petroleum, and carbon bisulphide, easily in alcohol, ether, benzene, and boiling water. It is dissolved by alkalis to a yellowish-red solution, and reprecipitated by acids. The *potassium salt* crystallises in yellow needles, the *ammonium salt* in yellowish-white needles, and the *silver salt* in greenish-yellow scales. By treating an aqueous solution of nitrocresol with bromine, *dibromonitrocresol* is obtained, crystallising in yellowish needles, melting at  $91\text{--}92^\circ$ . It is sparingly soluble in water and light petroleum, easily so in alcohol. *Amidocresol*,  $\text{C}_6\text{H}_3(\text{OH})\text{Me}(\text{NH}_2)$  [ $\text{OH} : \text{Me} : \text{NH}_2 = 1 : 2 : 5$ ], is obtained by the reduction of the nitro-body with tin and hydrochloric acid. It melts at  $159\text{--}161^\circ$ , and is identical with that described by Wallach (Abstr., 1883, 329). *Trinitro-orthocresol* was obtained by dissolving nitrotoluidine in two molecular proportions of nitric acid, diazotising, pouring the liquid product into moderately concentrated hot nitric acid, and boiling the whole. It crystallises in thick orange-yellow prisms, melting at  $102^\circ$ . It is sparingly soluble in cold water, easily so in alcohol, ether, acetone, acetic ether, and chloroform. Its constitution must be either [ $\text{OH} : \text{Me} : \text{NO}_2 : \text{NO}_2 = 1 : 2 : 4 : 5 : 6$ ,  $1 : 2 : 3 : 4 : 5$ , or  $1 : 2 : 3 : 5 : 6$ ] the authors think the first most probable. Alkalis decompose it with formation of a nitrite; with aniline it yields diazoamidobenzene. It forms molecular compounds with hydrocarbons like benzene and naphthalene; the compound with naphthalene crystallises in yellowish needles, which soften at  $102^\circ$ , and melt at  $106^\circ$ .

The authors are now investigating the reactions of *metamidocresol*, from which they have obtained a number of colouring matters.

L. T. T.

**Derivatives of Propylphenylamine.** By A. FRANCKSEN (*Ber.*, **17**, 1220—1231).—Propylphenylamine,  $\text{C}_6\text{H}_4\text{Pr}.\text{NH}_2$ , was prepared according to the directions given by Louis (*Ber.*, **16**, 105). Contrary to Louis' statements, the author has obtained the *hydrochloride* of this base in the form of white crystalline scales, soluble in water and alcohol, sparingly so in ether, and melting at  $203\text{--}204^\circ$ . The *platinochloride* crystallises in small bright yellow scales. The *hydrobromide* crystallises in glittering white scales, easily soluble in water and alcohol, and

melting at  $213^{\circ}$ . The *hydriodide*,  $\text{C}_3\text{H}_7\cdot\text{C}_6\text{H}_4\cdot\text{NH}_3\text{I}$ , forms small white scales, soluble in water, alcohol, and ether, but becoming rapidly discoloured on exposure to the air.

*Dipropylphenylthiocarbamide*,  $\text{CS}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Pr})_2$ , is obtained by digesting an alcoholic solution of the free base with carbon bisulphide. It crystallises in glittering white scales, sparingly soluble in cold alcohol, easily so in boiling alcohol, ether, and carbon bisulphide, and melting at  $138^{\circ}$ . *Propylphenylthiocarbamide*,  $\text{NH}_2\cdot\text{CS}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Pr})$ , was prepared by evaporating an aqueous mixture of propylphenylamine hydrochloride and ammonium thiocyanate. It crystallises in minute glittering white needles, easily soluble in ether and boiling alcohol, and melting at  $159^{\circ}$ .

*Propylphenylthiocarbimide*,  $\text{C}_6\text{H}_4\text{Pr}\cdot\text{NCS}$ , was obtained by Hofmann's reaction, by heating dipropylphenylthiocarbamide with a very concentrated solution of phosphoric acid (containing about 60 per cent. anhydride). It is a colourless oil which turns yellowish on exposure to the air. It boils at  $263^{\circ}$ , but is volatile in a current of steam. It is easily soluble in alcohol and ether.

*Dipropylphenylcarbamide*,  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Pr})_2$ , is obtained in almost theoretical quantity when propylphenylamine is heated with carbamide at  $150$ — $170^{\circ}$ . It forms a pure white crystalline mass, consisting of groups of needles. It is sparingly soluble in cold alcohol, easily so in boiling alcohol and in ether. It melts at  $205^{\circ}$ . It may also be prepared by treating a solution of propylphenylamine in benzene with phosgene gas, and in small quantity by the action of potassium thiocyanate on propylphenylamine sulphate. *Monopropylphenylcarbamide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Pr}$ , was prepared by mixing an aqueous solution of propylphenylamine hydrochloride with potassium isocyanate in the cold, and then warming the mixture gently. A small quantity of an oily base is formed and must be skimmed off the surface, and the aqueous solution evaporated. The di-substituted carbamide is always formed in this reaction, especially if the two solutions are not kept cool during the mixing. Monopropylphenylcarbamide forms colourless crystalline scales, which are easily soluble in boiling alcohol, very sparingly in cold alcohol, ether, and water. It melts at  $143^{\circ}$ .

*Dipropylphenylguanidine*,  $\text{NH}:\text{C}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Pr})_2$ , is obtained by heating an alcoholic solution of dipropylphenylthiocarbamide with excess of ammonia and lead oxide; the filtrate from the lead sulphide is mixed with water whilst still warm, and on cooling the guanidine crystallises out in small white needles. It is easily soluble in ether and boiling alcohol, and melts at  $113^{\circ}$ . The *platinochloride* forms a yellowish-brown amorphous powder. *Phenyldipropylphenylguanidine*,  $\text{NPh}:\text{C}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Pr})_2$ , is prepared by heating an alcoholic solution of dipropylphenylthiocarbamide with excess of aniline and lead oxide. It forms a yellowish resinous mass, easily soluble in ether, benzene, and boiling alcohol. *Tripropylphenylguanidine*,  $\text{NC}_6\text{H}_4\text{Pr}:\text{C}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Pr})_2$ , is prepared in a similar manner, propylphenylamine being substituted for aniline. It was not obtained in a crystalline form. Its *platinochloride* forms a brown amorphous powder, sparingly soluble in alcohol. In analogy with tri-substituted guanidines, tripropylphenyl-



guanidine, when heated with carbon bisulphide at 190—200°, splits up into dipropylphenylthiocarbamide and propylphenylthiocarbimide.

*Carbodipropylphenylimide*,  $C(N.C_6H_4Pr)_2$ , is obtained by heating a solution of dipropylphenylthiocarbamide in benzene with excess of lead oxide. It crystallises in clusters of needles, having an odour somewhat resembling that of oil of mustard. It melts at 168°. The *hydrochloride* forms white crystalline flakes. The imide is converted into the corresponding carbamide,  $CO(NH.C_6H_4Pr)_2$ , if its solution in dilute alcohol be heated for a short time on the water-bath. Heated with carbon bisulphide at 190° it yields propylphenylthiocarbimide. Heated with propylphenylamine in benzene solution, it gives tripropylphenylguanidine. Attempts to obtain dipropylphenylcarbamide by treatment of the imide with sulphuretted hydrogen were unsuccessful.

*Propylphenyl cyanide*,  $C_6H_4Pr.CN$ , was prepared by heating propylphenylthiocarbimide with freshly reduced copper powder at 220°. The copper rapidly blackens, and the odour of an isocyanide becomes perceptible, but after a time gives place to that of the nitrile. Propylphenyl cyanide is a colourless oil of aromatic odour, and boils at 227°. It is converted into the corresponding benzoic acid by heating it with excess of hydrochloric acid at 200°. The propylbenzoic acid thus obtained melts at 137°, and resembles in all its properties Paterno and Spica's para-propylbenzoic acid (*Ber.*, 10, 1746), obtained by the oxidation of para-propylisopropylbenzene, and for which they found the melting point 138—139. It is thus clear that the cyanide, and consequently the propylphenylamine investigated, are para-compounds.  
L. T. T.

**Constitution of Amidoisobutylbenzene.** By A. PAHL (*Ber.*, 17, 1232—1245).—The author has employed two methods for determining the relative position of the two side groups in this compound: A,—its conversion into a diazo-salt, thence into iodoisobutylbenzene, and the oxidation of this compound to an iodobenzoic acid. B,—by the successive conversion of the amine into di-isobutylphenylthiocarbamide, isobutylphenylthiocarbimide, isobutylphenyl cyanide, isobutylbenzoic acid, and finally the oxidation of this last-named body into one of the three well-characterised phthalic acids.

The isobutylphenylamine employed was prepared by acting on a mixture of isobutyl alcohol and aniline with zinc chloride, and was identical with that obtained by Studer by simply heating a mixture of isobutyl alcohol and aniline at 230°.

A. *Iodoisobutylbenzene*,  $C_6H_4I.C_4H_9$ , was obtained by the conversion of the hydrochloride of the amine into the diazo-salt, treating the solution of this salt with excess of hydriodic acid, and heating to boiling. It forms an easily fusible colourless crystalline mass, which boils at 255—256° (corr.), and volatilises in a current of steam. An attempt was made to oxidise this substance with chromic acid in acetic solution, but the results were not satisfactory; by heating the iodoisobutylbenzene with excess of nitric acid of sp. gr. 1.12 at 200°, however, it is converted into *iodobenzoic acid*. This sublimes easily in white nacreous scales, melting at 262°. Its methyl salt crystallises

in needles which melt at  $115^{\circ}$ . It is thus clear that the iodobenzoic acid in question is identical with the paraiodobenzoic acid of Schmidt and Schultze.

*B. Di-isobutylphenylthiocarbamide*,  $\text{CS}(\text{NH}.\text{C}_6\text{H}_4.\text{C}_4\text{H}_9)_2$ , was obtained by digesting an alcoholic solution of isobutylphenylamine with carbon bisulphide. It crystallises in beautiful white groups of needles, insoluble in water, sparingly soluble in boiling alcohol, easily so in boiling ether and benzene. It melts at  $192.5^{\circ}$ , and is converted into *isobutylphenylthiocarbimide*,  $\text{C}_4\text{H}_9.\text{C}_6\text{H}_4.\text{NCS}$ , by the action of syrupy phosphoric acid; this crystallises in needles melting at  $42^{\circ}$ , and boils at  $272^{\circ}$ . It is very soluble in alcohol and ether.

*Isobutylphenyl cyanide*,  $\text{C}_4\text{H}_9.\text{C}_6\text{H}_4.\text{CN}$ , obtained by Weith's method by heating the thiocyanate with powdered copper at  $200^{\circ}$ , forms a thick colourless liquid which boils at  $238^{\circ}$ , and does not solidify at  $-15^{\circ}$ . A vapour-density made in V. Meyer's apparatus gave 5.35 instead of 5.51 required by theory.

*Isobutylbenzoic acid*,  $\text{C}_4\text{H}_9.\text{C}_6\text{H}_4.\text{COOH}$ , was obtained by the saponification of the cyanide with alcoholic potash. It forms a white crystalline mass, which sublimes in long flat needles. It melts at  $161^{\circ}$ , and is easily soluble in alcohol and ether, very sparingly so even in boiling water. It forms characteristic salts which, with the exception of those of the alkalis, are insoluble, or nearly so, in water. The *silver salt* forms a white flocculent precipitate; the *barium salt* is easily soluble in boiling water, sparingly so in cold; the *calcium salt* forms a crystalline precipitate, which dissolves in boiling water and crystallises out again on cooling; the *methyl salt* is colourless and boils at  $247^{\circ}$ . Subjected to oxidation by an alkaline permanganate solution, isobutylbenzoic acid yielded *terephthalic acid*. From this result, and the iodobenzoic acid obtained by method A, it is clear that the isobutylphenylamine employed, and consequently that obtained by Studer, is the para-compound.

The author has also prepared the following derivatives:—*Di-isobutylphenylcarbamide*,  $\text{CO}(\text{NH}.\text{C}_6\text{H}_4.\text{C}_4\text{H}_9)_2$ , was obtained by passing carbon oxychloride into a solution of the original amine in benzene and also from the corresponding thiocarbamide already described. It crystallises in colourless needles, which melt at  $283\text{--}284^{\circ}$ , and are easily soluble in boiling alcohol, very sparingly so in water.

*Di-isobutylphenylguanidine*,  $\text{NH}:\text{C}(\text{NH}.\text{C}_6\text{H}_4.\text{C}_4\text{H}_9)_2$ , was obtained by treatment of the thiocarbamide with ammonia and lead oxide. It crystallises in colourless flakes, melting at  $173^{\circ}$ , and is easily soluble in hot alcohol and benzene. The *platinochloride* forms a yellow crystalline precipitate.

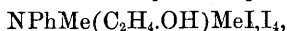
*Tri-isobutylphenylguanidine*,  $\text{C}_4\text{H}_9.\text{C}_6\text{H}_4.\text{N}:\text{C}(\text{NH}.\text{C}_6\text{H}_4.\text{C}_4\text{H}_9)_2$ , was prepared in a manner similar to the substance last described, except that isobutylphenylamine took the place of ammonia. It crystallises in small white needles, which melt at  $163\text{--}164^{\circ}$ , and are easily soluble in boiling alcohol and benzene. The *platinochloride* is a bright yellow crystalline precipitate. Heated with carbon bisulphide, this guanidine forms di-isobutylphenylcarbamide and isobutylphenylthiocarbimide.

*Carbodi-isobutylphenylimide*,  $\text{C}(\text{N}.\text{C}_6\text{H}_4.\text{C}_4\text{H}_9)_2$ , was prepared from

the di-substituted thiocarbamide by the action of lead oxide. The crystals melt at  $189^{\circ}$ , and are easily soluble in boiling benzene or toluene, sparingly so in boiling alcohol. Its solution in dilute alcohol easily yields the di-substituted carbamide when heated, and with ammonia gives di-isobutylphenylguanidine. When heated with carbon bisulphide at  $170^{\circ}$ , it yields isobutylphenylthiocarbimide.

L. T. T.

**Aromatic Alkines.** By W. LAUN (*Ber.*, **14**, 675—679).—*Methylphenylethylalkine*,  $\text{NPhMe.C}_2\text{H}_4\text{OH}$ , is obtained as hydrochloride, by heating equal molecular weights of methylaniline and ethylene chlorhydrin in sealed tubes at  $100^{\circ}$  for 35 hours. The free base is a colourless liquid of aniline-like odour; it boils at  $218\text{--}219^{\circ}$  under 110 mm. pressure, but cannot be distilled unchanged at the ordinary pressure, has sp. gr. 1.08065 at  $0^{\circ}$ , and is nearly insoluble in water. By long exposure to air, it is converted into a viscid blue syrup, soluble in water or alcohol with blue colour. The sulphate and nitrate could only be crystallised with great difficulty; neither platinochloride nor aurochloride could be prepared, the base precipitating both gold and platinum from their solutions. By heating the base with methyl iodide, the additive-compound,  $\text{NPhMe}(\text{C}_2\text{H}_4\text{OH})\text{MeI}$ , is obtained, crystallising in colourless tables and plates; treated with alcoholic solution of iodine, it yields a periodide,



crystallising in lustrous plates, and melting with decomposition at  $87^{\circ}$ .

*Phenyldiethylalkine*,  $\text{NPhEt.C}_2\text{H}_4\text{OH}$ , prepared from ethylaniline and ethylene chlorhydrin, closely resembles the foregoing compound, but distils unaltered at  $267\text{--}268.5^{\circ}$  under the ordinary pressure.

*Methylphenylpropylalkine*,  $\text{NMePh.C}_3\text{H}_6\text{OH}$ , prepared from methylaniline and propylene chlorhydrin, boils at  $262^{\circ}$ .

*Ethylphenylpropylalkine*,  $\text{NEtPh.C}_3\text{H}_6\text{OH}$ , prepared from ethylaniline and propylene chlorhydrin, is a colourless substance of very weak basic properties; it boils at  $261\text{--}263^{\circ}$ .

*Benzaldipiperyl*,  $\text{CHPh}(\text{C}_5\text{H}_{10}\text{N})_2$ , is obtained by long-continued heating of a mixture of benzaldehyde and piperidine in sealed tubes. It forms lustrous transparent prisms, of faint odour, recalling both its components, melts at  $80\text{--}81^{\circ}$ , and is destitute of basic properties. It is readily reconverted into benzaldehyde and piperidine by dilute acids, or by a few minutes' boiling with water.

A. J. G.

**Nitration of Benzene Derivatives.** By E. NÖLTING and A. COLLIN (*Ber.*, **14**, 261—268).—It is well known that, in the nitration of mono-substitution products of benzene, the para-disubstitution product is principally formed, together with small quantities of the ortho- and, quite exceptionally, traces of the meta-compounds, when the primary side group is of a basic ( $\text{NH}_2$ ), neutral ( $\text{CH}_3$  or a halogen), or only slightly acid ( $\text{OH}$ ) character; but that when this primary group is of a distinctly acid character, the meta-compound is that chiefly obtained. Hübner and Frerichs (*Ber.*, **10**, 1716), and Mears (*Ber.*, **9**, 744), have shown that if the basicity of the  $\text{NH}_2$ -group is

neutralised by combination with a strong acid, or by substitution of one of its hydrogen-atoms by an acid radical, the formation of meta-bisubstitution products takes place simultaneously with that of para- and ortho-derivatives. In the present communication, the authors show that by the use of strong acid solvents in large excess, when nitrating amido-derivatives, the formation of meta-derivatives can be determined, in some cases even to the exclusion of that of para- and ortho-derivatives.

*Aniline.*—Hübner and Frerichs have shown that aniline dissolved in 100 per cent. sulphuric acid (66° Baumé), and nitrated with a mixture of strong nitric and sulphuric acids, yields a mixture of the three isomeric nitranilines. The authors, by using a very large excess of sulphuric acid (50 parts) have succeeded in increasing the proportion of metanitrilaniline, but the para-body was always present.

*Acetanilide.*—The nitration of this body may be conveniently carried out on a considerable scale as follows:—590 grams (1 mol.) of nitric acid of sp. gr. 1.478 (or the corresponding quantity of acid of sp. gr. 1.400), mixed with 1200 grams of sulphuric acid, is allowed to flow slowly into a solution of 1 kilo. acetanilide in 4 kilos. sulphuric acid, cooled by ice and salt. The whole is allowed to stand for some time and then poured into iced water, when paranitracetanilide separates out in pale yellow flakes, which, after one recrystallisation, have the correct melting point, 207°. The yield is over 95 per cent., and the authors have worked with quantities up to 2 kilos. of acetanilide. Paranitrilaniline is obtained from the aceto-compound by saponification with concentrated sulphuric acid: a trace of ortho-nitrilaniline is always present in the mother-liquors. By largely increasing the proportion of sulphuric acid used as a solvent, small quantities of metanitracetanilide are produced, but the para-body is always the principal product.

*Paratoluidine*, dissolved in 10 parts of sulphuric acid, and nitrated in a similar manner, yields a mixture of the two isomeric nitrotoluidines of melting points 114° [ $\text{NH}_2 : \text{NO}_2 : \text{Me} = 1 : 2 : 4$ ] and 78° [ $1 : 3 : 4$ ], the latter always being in excess. If the sulphuric acid be increased to 15—20 parts, the [ $1 : 3 : 4$ ] derivative alone is produced.

*Paracetotoluide*, dissolved in 4 parts sulphuric acid, yields the same nitroacetotoluide—of m. p. 92°, and yielding nitrotoluidine of m. p. 114° and constitution [ $\text{NH}_2 : \text{NO}_2 : \text{CH}_3 = 1 : 2 : 4$ ]—obtained by Beilstein and Kuhlberg by adding paracetotoluide to fuming nitric acid. The yield is good. If 10 parts of sulphuric acid be used, a mixture of the two isomerides [ $1 : 2 : 4$ ] and [ $1 : 3 : 4$ ] is obtained; and if the acid be increased to 20 parts, the proportion of the latter is increased, but this could not be obtained as the sole product even by still further increasing the proportion of sulphuric acid used.

*Orthotoluidine* in 10 parts sulphuric acid yields a nitro-derivative, melting at 107°, and which the authors show (p. 1007) to be  $\text{C}_6\text{H}_3(\text{NH}_2)\text{Me}(\text{NO}_2)[\text{NH}_2 : \text{Me} : \text{NO}_2 = 1 : 2 : 5]$ . With more than 10 parts sulphuric acid, the reaction takes place less regularly.

*Orthacetotoluide* in 4 parts sulphuric acid gives a mixture of the two isomeric nitro-orthacetotoluides [ $\text{NHAc} : \text{Me} : \text{NO}_2 = 1 : 2 : 5$  and  $1 : 2 : 4$ ]; with 20 parts, exclusively the former.

*Metaxylylidine* in 10 parts sulphuric acid gives the nitroxylylidine [ $\text{NH}_2 : \text{Me} : \text{Me} : \text{NO}_2 = 1 : 2 : 4 : 5$ ], melting at  $123^\circ$ , and already described by Fittig, Ahrens, and Matheides (*Annalen*, **147**, 18).

*Metaceto-xylylide* in 10 parts sulphuric acid yields the aceto-derivative corresponding with the above-named nitro-xylylidine; with 4 parts sulphuric acid, this is mixed with the [ $1 : 2 : 4 : 6$ ] derivative obtained when fuming nitric acid alone is used.

*Parabromaniline* in 10 parts sulphuric acid yields a new *para*-bromonitraniline, melting at  $131\text{--}132^\circ$ , and having the constitution [ $\text{NH}_2 : \text{NO}_2 : \text{Br} = 1 : 3 : 4$ ]. It crystallises from alcohol in flat needles, is easily soluble in alcohol, ether, acetic acid, ethyl acetate, and chloroform, sparingly so in water. Treated in acetic solution with excess of bromine, it yields the tribromonitraniline, melting at  $102.5^\circ$ , already obtained by brominating metanitriline, thus establishing the correctness of the above formula.

*Ethylacetanilide* in 5 parts of sulphuric acid yields *paranitro-ethylacetanilide*, melting at  $118^\circ$ . When saponified with hydrochloric acid, this yields *paranitroethylaniline*; it crystallises from alcohol in pale yellow prisms, showing a bluish-violet fluorescence, and melting at  $96^\circ$ . By reduction with tin and hydrochloric acid, a monethyl-phenylenediamine is obtained, which yields a hydrochloride, crystallising in white scales, soluble in water and alcohol. This diamine has all the characteristics of a *para*-diamine, and yields safranine, indophenol, and quinone; thus proving the *para*-position of the nitro-group.

*Dimethylaniline* in 20 parts of nitric acid yields *paranitrodimethylaniline*. No isomerides could be detected.

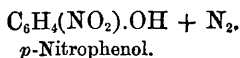
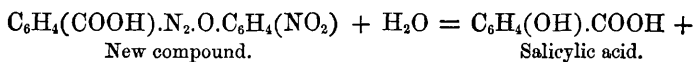
These researches show the great influence which the solvent has in determining the position of the hydrogen-atom substituted during the process of nitration.

L. T. T.

**Introduction of the Diazo-group into so-called Aromatic Para-compounds.** By P. GRIESS (*Ber.*, **17**, 338—341).—In reference to the statements of Liebermann and v. Kostanecki (this vol., p. 736), the author points out that he some time ago (*Abstr.*, 1882, 182) proved the incorrectness of the generally received idea that the diazo-group always enters phenols in the *para*-position relatively to the hydroxyl-group. After the author had found that of the three diamidobenzenes and their homologues only the meta-compounds are capable of uniting with the diazo-compounds to form dyes, he investigated the action of the phenols in this respect, but found that although the same is the case with the three dihydroxybenzenes, no such regularity exists with regard to other di-substituted derivatives containing a hydroxyl-group. As regards the statement of Nölting and Witt (*Ber.*, **17**, 77, this vol., p. 742) "that it has hitherto always been accepted as a fact that amido- and oxyazo-derivatives can only be formed by the action of diazo-compounds on phenols and amines when the *para*-position in these is still unoccupied," the author draws attention to the fact that he has always contested this, and long ago proved its incorrectness.

Paranitrophenol is capable of entering into combination with

certain diazo-derivatives, but the compounds so obtained approach the diazo-compounds in character much more nearly than they do to the azo-compounds. When a cold concentrated and slightly alkaline solution of paranitrophenol is treated with the nitrate of orthodiazobenzoic acid, it yields a substance crystallising in minute white scales; this is easily soluble in alcohol, but insoluble in ether, and is at once decomposed by boiling water according to the equation—



An analogous but less stable compound is obtained when orthonitrophenol is substituted for the para-compound, and is now under investigation. L. T. T.

**Action of Hydrochloric Acid on Amidoazo-compounds.** By O. WALLACH and A. KÖLLIKER (*Ber.*, **17**, 395—399).—Amidoazobenzene is rapidly decomposed by hydrochloric acid at 100°, the chief products of the decomposition being aniline, paraphenylenediamine, and di-, tri-, and tetra-chloroquinol. This decomposition can only be accounted for on the assumption that the hydrochloric acid acts like a mixture of free hydrogen and free chlorine. The formation of induline by the action of strong hydrochloric acid on amidoazobenzene is due to a secondary reaction. W. C. W.

**Diazoamidobenzene.** By B. FISCHER (*Ber.*, **17**, 641—642).—In the preparation of amidoazobenzene, sodium acetate was added to the mixture of aniline, hydrochloric acid, and sodium nitrite in the expectation that the reaction would be facilitated. It was found, however, that under these circumstances diazoamidobenzene was obtained, and not amidoazobenzene. When sodium hydroxide is added, however, instead of the acetate, amidoazobenzene is produced. A. J. G.

**Azophenols.** By R. BOHN and K. HEUMANN (*Ber.*, **17**, 272—276).—The authors have already shown (*Abstr.*, 1883, 583) that on nitrating parazophenol the azo-group is eliminated and dinitrophenol formed. They have now further investigated the behaviour of azophenols towards various reagents. Parazophenolmonosulphonic acid was introduced into warm nitric acid, and the product precipitated with water: [1 : 2 : 4] *dinitrophenol* was obtained, melting at 113—114°, showing that both the azo- and sulphonic-groups had been removed. Orthazophenol, melting at 171°, prepared by fusing orthonitrophenol with potash, was nitrated in acetic solution: picric acid was obtained, showing that here also the azo-group had been destroyed. The author believes that the formation of a tri- instead of a di-nitro-derivative was probably due to the reaction having accidentally become more violent. By chlorinating parazophenol in

acetic solution, *trichlorophenol*,  $C_6H_2Cl_3.OH$ , was obtained. On first passing the stream of chlorine, a slight precipitate, consisting of dark violet needles, was produced; this proved to be a modified crystalline form of *parazophenol*. Chlorine passed into an acetic solution of *orthazophenol* yielded *trichlororthazophenol*, the behaviour of the ortho- and para-derivatives to chlorine being thus quite different. *Trichlororthazophenol* crystallises in long, reddish-yellow needles, which melt at  $235^\circ$ , and sublime unchanged. It is soluble in benzene, sparingly so in alcohol and light petroleum, and crystallises from the latter in yellow silky needles. It dissolves in alkalis with red coloration, and gives a deep red colour with ferric chloride or other oxidising agents.

L. T. T.

**Hydrazobenzene and Benzidine.** By D. STERN (*Ber.*, 17, 379—381).—The product of the action of hydrazobenzene on benzoic chloride is partly soluble in alcohol. The crystalline residue, consisting of *dibenzoylbenzidine*,  $NPhBz.NPhBz$ , is insoluble in the usual solvents, but dissolves in hot nitrobenzene. The colourless crystals sublime without decomposition. This compound is also formed by the action of benzoic chloride on benzidine.

*Di-formylbenzidine*,  $CHO.NH.C_6H_4.NH.CHO$ , prepared by the action of formic acid on hydrazobenzene, resembles the preceding compound. *Monacetohydrazobenzene* is formed by bringing together acetic anhydride and hydrazobenzene at the ordinary temperature. It is deposited from alcohol in needle-shaped crystals melting at  $159^\circ$ , soluble in water. It is decomposed by heat into azobenzene and acetanilide.

W. C. W.

**Action of Bibasic Organic Acids on Hydrazobenzene.** By E. BANDROWSKI (*Ber.*, 17, 1181—1185).—Beilstein's statement that organic acids have no action on hydrazobenzene is incorrect. On heating a mixture of hydrazobenzene (1 mol.) with phthalic anhydride (2 mols.) at  $130^\circ$  for three hours, a reaction takes place. The product is partly soluble in benzene and alcohol. The insoluble residue consists of diphthalyl-diparabenzidine,  $C_{28}H_{16}N_2O_4$ , and the solution contains azobenzene, phthalanile, and a substance melting at  $194^\circ$ , probably the diphthalyl of parorthobenzidine.

*Diphthalyl-diparabenzidine* is deposited from its solution in hot nitrobenzene in yellow crystals which melt above  $360^\circ$ . It dissolves in strong sulphuric acid; if the solution is heated to  $140^\circ$ , it splits up into diparabenzidine and phthalic anhydride. The compound may be easily prepared by heating a mixture of these two bodies. Diphthalyl-diparabenzidine dissolves in fuming nitric acid; and on diluting the solution with water, a dinitro-product,  $C_{28}H_{14}(NO_2)_2N_2O_4$ , is precipitated. Alcohol precipitates it from its solution in nitrobenzene as a crystalline powder.

An energetic reaction takes place on heating a mixture of hydrazobenzene and anhydrous oxalic acid. On extracting the crude product with alcohol, a crystalline compound goes into solution, and a violet-grey residue remains having the composition  $C_{16}H_{12}N_2O_4$ ; it is insoluble in the usual solvents, but dissolves in strong sulphuric acid.

The addition of water to the solution produces an amorphous precipitate, which dissolves in alkalis, forming a deep red liquid. The colour is destroyed by zinc-dust, but reappears on exposure to the air.

W. C. W.

**Paramidoacetanilide, and some New Azo-derivatives.** By R. NIETZKI (*Ber.*, 17, 343—346).—By the reduction of paranitracetanilide with iron and a little acetic acid, the author has obtained *paramidoacetanilide*. Hitherto when dealing with nitrated anilides, the action has gone further, acetic acid being always eliminated. The author believes this to be due to the use of too energetic reducing agents. *Paramidoacetanilide* crystallises in long colourless concentrically-grouped needles, very sparingly soluble in cold water, easily so in boiling water, alcohol, and ether: it melts at  $161^{\circ}$ . It acts as a monacid base forming crystalline salts; its platinochloride crystallises in yellow, sparingly soluble needles. When boiled with dilute acids, it is readily decomposed into acetic acid and paraphenylenediamine.

If the diazo-compound is added to an alkaline solution of  $\beta$ -naphthol-disulphonic acid, a body crystallising in glistening golden scales, and having the probable constitution  $\text{NH}\bar{\text{A}}\text{c}.\text{C}_6\text{H}_4.\text{N}_2.\text{C}_{10}\text{H}_7(\text{HSO}_3)_2.\text{OH}$ , is formed. On boiling this with dilute sulphuric acid, the acetyl-group is removed and a purplish-red colouring matter is obtained which can again be further diazotised. If this is treated with  $\beta$ -naphthol-disulphonic acid, it yields a colouring matter crystallising in green iridescent needles, and dyeing wool and silk a deep indigo-blue: the colour is however unstable if exposed to the light, soon changing into a brownish-violet.

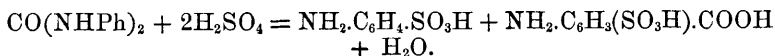
Paradiazacetanilide and aniline yield *acetyldiamidoazobenzene*,  $\text{NH}\bar{\text{A}}\text{c}.\text{C}_6\text{H}_4.\text{N}_2.\text{C}_6\text{H}_4.\text{NH}_2$ , crystallising in golden-yellow scales which melt at  $212^{\circ}$ . Acids turn it red. The hydrochloride forms silver-grey scales. Boiling with dilute sulphuric acid converts the acetyl compound into symmetric *paradiamidoazobenzene*. This substance has also been described by Mixter (this vol., 665) under the name of *parazoaniline*. It crystallises from alcohol in long, golden-yellow needles, easily soluble in alcohol, sparingly so in benzene and light petroleum. It forms two series of salts, those with two proportions of the acid being red in colour, those with one equivalent of acid green. The dihydrochloride is precipitated from an alcoholic solution of the base by excess of hydrochloric acid in the form of very dark green iridescent needles.

L. T. T.

**Action of Sulphuric Acid on Carbanilide.** By W. HENTSCHEL (*Ber.*, 17, 1287—1289).—Pure carbanilide dissolves in cold concentrated sulphuric acid without discoloration, and the solution may be kept for days without change. But if carbanilide be digested on the water-bath for about half an hour with about five times its weight of acid, although there is no apparent reaction, a change has taken place. The product, poured into water and treated with barium carbonate, yields barium sulphanilate and the barium salt of an acid having the formula  $\text{C}_7\text{H}_7\text{NSO}_6$ . The free acid is easily soluble in water, and the



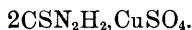
author believes it to be an amidosulphobenzoic acid, the reaction being as follows:—



L. T. T.

**Derivatives of Thiocarbamide.** By B. RATHKE (*Ber.*, **17**, 297—309).—The author has carefully investigated some of the compounds which thiocarbamide forms with metallic salts, as they seem to prove that many of the so-called molecular compounds are really true chemical compounds.

The author has already (*Abstr.*, 1883, 166) described a copper compound of thiocarbamide obtained by adding cupric chloride to a solution of thiocarbamide. Prätorius and Seidler have since described a similar compound to which they have ascribed the formula



This is incorrect, as the copper contained in the compound must be monovalent, since sulphuretted hydrogen precipitates  $\text{Cu}_2\text{S}$  and not  $\text{CuS}$ . If cupric chloride is added to a solution of thiocarbamide as long as a precipitate is formed, the latter is found to consist of minute white needles of the formula  $\text{CSN}_2\text{H}_4\cdot\text{CuCl}$ : the colourless and strongly acid filtrate contains the compound of 1 mol. thiocarbamide and 1 atom of chloride described by Claus (*J. pr. Chem.*, **21**, 146). Cupric sulphate yields similar compounds. Cuprous chloride yields three compounds containing respectively 1, 2, and 3 mols. of thiocarbamide to the group  $\text{CuCl}$ . The first of these is insoluble in water, the third soluble, whilst excess of water splits up the second into equal proportions of the first and third. The body  $3\text{CSN}_2\text{H}_4\cdot\text{CuCl}$  is obtained by adding a dilute solution of cupric chloride to a boiling solution of thiocarbamide as long as the precipitate formed is quickly redissolved; also, by digesting together the calculated quantities of these two substances; or by covering pieces of copper-foil with a solution of thiocarbamide and adding small quantities of hydrochloric acid from time to time, when a copious evolution of hydrogen takes place, and the solution contains the substance in question. It forms large colourless and strongly refractive crystals belonging to the quadratic system. Its solution has an alkaline reaction. It is reprecipitated unchanged from its solution by soluble chlorides. Zinc precipitates copper from its solutions; ammonia and sodium hydroxide and carbonate give white precipitates which gradually blacken, becoming converted into cuprous sulphide: sulphuretted hydrogen causes a precipitation of cuprous sulphide, but only *very* slowly. The body  $\text{CSN}_2\text{H}_4\cdot\text{CuCl} + \frac{1}{2}\text{H}_2\text{O}$  is obtained if excess of cupric chloride is used, and forms a voluminous white precipitate consisting of minute needles. It is also obtained by digesting together the calculated quantities of thiocarbamide and cuprous chloride. It loses its water in the desiccator, becoming at the same time very slightly greyish-blue.  $2\text{CSN}_2\text{H}_4\cdot\text{CuCl}$  is obtained by uniting the two previously-described compounds, and is again decomposed into these two by excess of water. It crystallises in needles. Cupric sulphate added in excess to a solu-

tion of thiocarbamide precipitates a yellow oil which solidifies on exposure to the air. If this substance is dissolved in a boiling solution of thiocarbamide a body crystallises out on cooling in long needles having the formula  $5\text{CSN}_2\text{H}_4, \text{Cu}_2\text{SO}_4 + 2\text{H}_2\text{O}$ . Analogous compounds may be obtained containing cuprous nitrate or carbonate. In all these compounds half the sulphur is precipitated as cuprous sulphate on boiling the substance with dilute ammonia: the remainder of the sulphur can then be precipitated from the filtrate by ammoniacal silver nitrate.

The author believes all these compounds to be true *chemical* and not merely *molecular* compounds, for the following reasons:—(1.) Neither cuprous carbonate nor nitrate can exist in the free state. (2.) The soluble among these compounds (even that with mercuric chloride) have an alkaline reaction. (3.) Copper, when heated with thiocarbamide and hydrochloric acid, dissolves readily with evolution of hydrogen. (4.) Cuprous chloride, both in hydrochloric and ammoniacal solution, absorbs carbonic acid readily, but in these compounds it does not do so.

The author has also obtained analogous compounds with phenylthiocarbamide. If a little copper chloride be added to a solution of monophenylthiocarbamide in boiling water, the smell of phenylthiocarbamide becomes perceptible, and a yellow oil is precipitated. This oil solidifies on cooling, and, when recrystallised from alcohol, yields colourless crystals. The same substance is obtained by boiling cuprous chloride in a solution of monophenylthiocarbamide, and also by boiling the compound  $\text{CSN}_2\text{H}_4, \text{CuCl}$  with phenylthiocarbamide and water. Analysis showed the composition of this substance to be



It appears to lose its water of crystallisation at  $100^\circ$ , but also undergoes partial decomposition: it melts at  $144\text{--}145^\circ$ . Another compound of phenylthiocarbamide containing a larger proportion of cuprous chloride was also obtained. Diphenylthiocarbamide yields analogous compounds when treated with cuprous chloride.

The compounds of thiocarbamide which Reynolds has obtained with gold and platinum chlorides also belong to this class of bodies. The author has examined the gold chloride compounds and finds the gold to be present in the aurous state.

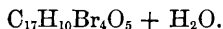
Salts of barium, magnesium, cobalt, nickel, manganese, zinc, iron as ferrous salt, and chromium, do not show any change in reaction of their neutral or acid solutions when mixed with thiocarbamide, but solutions of mercuric chloride and cyanide, silver chloride and nitrate, cadmium and thallium sulphates, and lead chloride become strongly alkaline when so treated, pointing to the formation of double compounds.

The author has replaced the metals in these compounds by ethyl (by treatment with ethyl iodide), and obtained the compound  $\text{HI}, \text{NH} : \text{C}(\text{NH}_2) \cdot \text{SEt}$ , which seems clearly to point to the metal being attached to the sulphur-atom. The proof is however not absolute, as the same compound is obtained when free thiocarbamide is treated with ethyl iodide.

L. T. T.

**Methylphthalimide.** By C. GRAEBE and A. PICTET (*Ber.*, 17, 1173—1175).—*Methylphthalimide*,  $\text{NMe} : \text{C} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{O} \end{smallmatrix} > \text{CO}$ , formed by the action of potassium phthalimide on methyl iodide at  $150^\circ$ , crystallises in silky needles which are soluble in alcohol and in hot water. Methylphthalimide melts at  $132^\circ$  and boils about  $277^\circ$ . On reduction with tin and hydrochloric acid it yields a base,  $\text{C}_9\text{H}_9\text{ON}$ , which melts at  $120^\circ$  and boils at  $300^\circ$ . It is deposited from an ethereal solution in large plates which dissolve freely in water, alcohol, ether, and chloroform. The *hydrochloride* is insoluble in ether and chloroform. The *aurochloride*,  $(\text{C}_9\text{H}_9\text{ON})_2\text{HAuCl}_4$ , forms beautiful crystals which melt under boiling water. In the dry state they melt at  $195^\circ$  with gradual decomposition.  
W. C. W.

**Pyrotartrylfluorescein.** By E. HJELT (*Ber.*, 17, 1280—1281).—The fluorescein of pyrotartaric acid was obtained by heating together 5 parts of tartaric acid, 9 parts resorcinol, and 18 parts sulphuric acid at  $150^\circ$ . This colouring matter forms a brownish-red crystalline powder,  $\text{C}_{17}\text{H}_{14}\text{O}_5 + \text{H}_2\text{O}$ , sparingly soluble in water, easily in dilute acids and alcohol. A concentrated alkaline solution is red, but when diluted shows beautiful yellow-green fluorescence. Its alkaline solution forms a basic salt with copper sulphate. The hydrochloric solution, if treated with bromine, yields pyrotartryleosin,



This forms a red flocculent precipitate. In dilute alkaline solution this substance shows no red colour, and has only a very slight fluorescence.  
L. T. T.

**Use of Dry Oxalic Acid in the Formation of Condensation-products.** By R. ANSCHÜTZ (*Ber.*, 17, 1078—1079).—Owing to the great affinity which anhydrous oxalic acid, obtained by heating oxalic acid at  $110^\circ$  until all its water of crystallisation is given off, has for water, the author has found it useful in the elimination of water from mixtures of substances which are capable of forming condensation-products. On heating 5 grams benzaldehyde and 11.5 of dimethylaniline together for two hours at  $110^\circ$ , no change takes place, but if 7.5 grams anhydrous oxalic acid are added, and the mixture heated for the same time at  $110^\circ$ , the product of condensation, leucomalachite-green, is formed in large quantities. In a similar way benzaldehyde, when heated with diphenylamine or benzyldiphenylamine, in presence of dry oxalic acid, yields condensation-products and phthalic anhydride, whilst resorcinol gives fluorescein. The water eliminated in this way does not, owing to the high temperature, combine to form water of crystallisation with the oxalic acid, but the oxalic acid remains unchanged. This property of dry oxalic acid is under further investigation.  
A. B.

**Orthamidobenzaldehyde.** By P. FRIEDLÄNDER and C. F. GÖHRING (*Ber.*, 17, 456—461).—Orthamidobenzaldehyde is prepared

by warming pure orthonitrobenzaldehyde (3 grams) with ferrous sulphate (50 grams) and ammonia. The mixture is distilled in a current of steam. About 30 per cent. of the aldehyde is deposited from the distillate on cooling to  $0^{\circ}$ , and the remainder is obtained by adding common salt to the mother-liquor, and extracting with ether. The properties of the compound have been previously described (*Ber.*, 15, 2004, 2572).

*Acetylorthamidobenzaldehyde*, prepared by warming the amidoaldehyde with pure acetic anhydride, is deposited from hot aqueous solutions in white needles, which melt at  $70^{\circ}$ .

Orthamidobenzaldehyde dissolves in strong hydrochloric acid, forming a red solution which, on the addition of platinum chloride, deposits yellow prisms of the platinochloride  $(C_7H_7NO)_2, H_2PtCl_6$ .

Amidobenzaldehyde is easily converted into a condensation-product,  $C_{14}H_{12}N_2O$ , by the action of dilute mineral acids. This compound forms tabular crystals, which melt at  $189^{\circ}$  when rapidly heated. It dissolves in strong acids, with regeneration of the amidoaldehyde.

$\beta$ -Carbostyrylcarboxylic acid,  $C_{10}H_7NO_3$ , is formed when orthamidobenzaldehyde is heated with a slight excess of malonic acid at  $120^{\circ}$ . It crystallises in needles, which melt above  $320^{\circ}$ , and are sparingly soluble in alcohol and acetic acid. Phosphorous pentachloride converts it into  $\alpha$ -chloro- $\beta$ -quinolinecarboxylic acid, which crystallises in needle-shaped crystals, melting at  $200^{\circ}$  with partial decomposition into chloroquinoline and carbonic anhydride. Boiling with alcoholic potash converts the chloroquinoline into  $\alpha$ -ethoxy- $\beta$ -quinolinecarboxylic acid, which melts at  $130^{\circ}$  and is rapidly decomposed by heat into ethylcarbostyryl and carbonic anhydride. W. C. W.

**Derivatives of Phenylacetaldehyde.** By C. FORRER (*Ber.*, 17, 982—985).—*Action of Phosphorous Pentachloride on Phenylacetaldehyde.*—The reaction takes place in the usual way, the oxygen of the aldehyde being replaced by two atoms of chlorine, with formation of *dichlorethylbenzene*,  $CH_2Ph.CHCl_2$ . It is a heavy liquid, smelling like turpentine, and rapidly decomposes with evolution of hydrochloric acid; by distillation it is completely decomposed. Heated at  $120^{\circ}$ , it is completely converted into  $\alpha$ -chlorostyrolene,  $CHPh:CHCl$ . When this is heated in a closed tube with alcoholic potash, an oil is obtained free from chlorine, and which on distillation gives phenylacetaldehyde again. This is the third *dichlorethylbenzene* :—

$C_6H_5.CCl_2.CH_3$   $\alpha$ -dichlorethylbenzene from acetophenone.

$C_6H_5.CCl.CH_2Cl$   $\alpha\omega$ -dichlorethylbenzene from styrolene.

$C_6H_5.CH_2.CHCl_2$   $\omega$ -dichlorethylbenzene from phenylacetaldehyde.

*Action of Nitric Acid on Phenylacetaldehyde.*—This reaction is of interest, since the reduction of the orthonitro-compounds should yield indole directly. Phenylacetaldehyde was treated at  $-10^{\circ}$  to  $-15^{\circ}$  with nitric acid. On neutralising, and distilling the resulting product with steam, a small quantity of an oil which crystallised out in plates was first obtained, and a second substance which crystallised out in fine needles. The first substance melted at  $106^{\circ}$ , and on reduction

with ammonia and zinc-dust yielded an oil, in too small a quantity for purification, but which gave all the characteristic reactions for indole. The second crystalline substance melted at 133—136°, yielded no indole on reduction, but on oxidation a nitrobenzoic acid which, from its melting point, is probably the paranitro-acid. This second substance is therefore probably paranitrophenylacetic acid.

A. B.

**Derivatives of Orthamidoacetophenone.** By A. BAEYER (*Ber.*, 17, 970—973).—In former unsuccessful attempts to obtain diethyl-indigo and dibenzyl-indigo from ethyl- and benzyl-amidoacetophenone, the author prepared several derivatives of orthamidoacetophenone.

*Orthoethylamidoacetophenone* is obtained by heating 16 grams amidoacetophenone with 32 grams ethyl bromide in a closed tube for 20 hours at 100°; the red product is freed from the excess of ethyl bromide, dissolved in water, treated with soda, and distilled in steam. The ethylamidoacetophenone is thus obtained as an oil, and is purified by being converted into the nitroso-compound, and regenerated by the action of stannous chloride. It forms a platinum-chloride,  $(\text{NHEt} \cdot \text{C}_6\text{H}_4 \cdot \text{COMe})_2 \cdot \text{H}_2\text{PtCl}_6$ .

*Orthobenzylamidoacetophenone* is obtained by heating two parts of amidoacetophenone with one part benzyl chloride at 100° for three hours. Crystallised from alcohol, it forms large yellow prisms, melting at 79—81°, readily soluble in carbon bisulphide, chloroform, benzene, and ether. It is a feeble base, and is precipitated from its acid solution by water.

*Orthonitrosobenzylamidoacetophenone*,  $\text{COMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{NO})\text{C}_7\text{H}_7$ , is obtained by the action of sodium nitrite on a solution in sulphuric acid. It forms long colourless needles, melting at 54—55°, and is soluble in alcohol and similar solvents. Benzyl-indigo cannot be obtained by the bromination of benzylamidoacetophenone, but by treating the nitroso-derivative with concentrated sulphuric acid, colouring matters of the nature of indigo are formed, probably consisting chiefly of indigo and benzyl-indigo. The formation of indigo is to be explained on the ground that the benzyl-group is detached by the action of sulphuric acid, for, on treating the nitroso-derivative with sulphuric acid, there is a strong odour of benzaldehyde.

A. B.

**Orthhydroxyphenylacetic Acid and its Derivatives.** By A. BAEYER and B. FRITSCH (*Ber.*, 17, 973—975).—The authors regret that as they have been working for some time on this acid they cannot accede to Salkowski's request (*Ber.*, 17, 504) that he be allowed to reserve the investigation of the isomeric hydroxyphenylacetic acids. Their method of preparing the acid and its internal anhydride, however, is quite different from his.

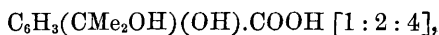
*Orthhydroxyphenylglyoxylic acid* is obtained by treating a solution of isatin in dilute soda with the calculated quantity of sodium nitrite, and slowly adding an excess of very cold dilute sulphuric acid. This solution of orthodiazophenylglyoxylic acid, when heated at 60°, gives off nitrogen, and the hydroxy-acid may be obtained by extraction with ether. It crystallises from a mixture of benzene and light petroleum in yellow needles, melting at about 44°. It is, how-

ever, impure, and contains salicylic acid. On treating this crude acid with sodium amalgam for several days, acidifying and extracting with ether, a crystalline compound is obtained, which appears to be orthhydroxymandelic acid. It is easily reduced by means of hydriodic acid to orthhydroxyphenylacetic acid.

*Orthhydroxyphenylacetic acid* crystallises from ether in colourless needles, melting at  $137^{\circ}$ , and its aqueous solution, like that of salicylic acid, gives a violet coloration with ferric chloride. On heating it, water is at first given off, and afterwards, at  $236-238^{\circ}$ , an oil distils over and crystallises. This is the lactone of *orthoxyphenylacetic acid*,  $C_6H_4\langle\begin{smallmatrix} CH_2 \\ -O- \end{smallmatrix}\rangle CO$ . It melts at  $49^{\circ}$ , boils at  $237^{\circ}$ , and in hot water is slowly converted into the acid, more quickly in presence of alkalis.

A. B.

**Action of Nitrous Acid on Amidohydroxypropyl- and Amidopropenyl-benzoic Acids.** By O. WIDMAN (*Ber.*, 17, 722-727).—*Hydroxypropylhydroxybenzoic acid*,



prepared by the action of nitrous acid on amidohydroxypropylbenzoic acid, crystallises in colourless flat needles or plates, melts at  $173^{\circ}$ , is sparingly soluble in cold water, moderately soluble in ether, very readily soluble in alcohol. Its aqueous solution gives a dark brown coloration with ferric chloride. It does not appear to suffer any change by boiling with hydrochloric acid; dissolved in sulphuric acid and precipitated with water, white shiny flocks are obtained, but there appears to be no formation of propenylhydroxybenzoic acid. In this respect the acid differs from the corresponding hydroxypropylbenzoic acid with its anido- and nitro-derivatives, all of which are converted into propenyl-compounds by heating with hydrochloric acid.

With amidopropenylbenzoic acid, the action of nitrous acid takes another course, the product of the reaction being *methylcinnoline-*

*carboxylic acid*,  $C_{10}H_8N_2O_2 = COOH.C_6H_3\langle\begin{smallmatrix} CMe \\ N:N \end{smallmatrix}\rangle CH$ . It crystallises

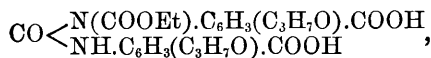
in small tables, or in thick rhombohedral-like crystals, melts with partial decomposition at about  $230^{\circ}$ , is insoluble in cold water, sparingly soluble in hot water or hot alcohol, readily soluble in boiling acetic acid. It yields salts with acids and bases. Together with this acid, a substance is formed in small quantity which crystallises in colourless rhombic plates, melting at  $157-158^{\circ}$ . It has not yet been obtained in quantity sufficient for careful examination.

A. J. G.

**Action of Ethyl Chloroformate on Amidohydroxypropylbenzoic Acid.** By O. WIDMAN (*Ber.*, 17, 1303-1308).—If an excess of ethyl chloroformate is poured over amidohydroxypropylbenzoic acid, and the mixture boiled for a few minutes, the whole solidifies, but no evolution of gas is perceptible. After allowing the excess of ethyl chloroformate to evaporate, the product is crystallised

from 50 per cent. acetic acid. *Hydroxypropylcarboxylphenylurethane*,  $C_{13}H_{17}NO_5$ , thus obtained, crystallises in flat colourless needles or prisms, which melt at  $167^\circ$ , with evolution of gas. The reaction is probably  $C_{10}H_{11}O_3.NH_2 + Cl.COEt = HCl + C_{10}H_{11}O_3.NH.COEt$ .

*Ethyl dihydroxypropyldicarboxyldiphenylallophanate*,



is obtained by heating the body just described with ethyl chloroformate in sealed tubes at  $120$ — $130^\circ$  for two hours. It may also be prepared directly from the amido-acid by using excess of chloroformate. It crystallises from acetic acid in plates, which melt above  $300^\circ$  with evolution of gas, and the residue resolidifies on cooling. This latter body appears to be identical with *dihydroxypropyldicarboxyldiphenylcarbamide*,  $CO[NH.C_6H_5(C_3H_7O).COOH]_2$ , obtained as follows: amidohydroxypropylbenzoic acid is heated with excess of ethyl chloroformate for four hours, hydrochloric acid being continuously evolved. The product is evaporated to dryness several times, first with water, and subsequently with alcohol; the residue is then washed with ether, and boiled with fuming hydrochloric acid, in which it slowly dissolves with evolution of gas; finally the solution is evaporated to dryness, and the residue boiled with water, when the carbamide-derivative remains undissolved. Crystallised from acetic acid, it forms small rhombic prisms, which melt at a very high temperature.

Several attempts were made to treat amidohydroxypropylbenzoic acid with excess of ethyl chloroformate in sealed tubes at  $115$ — $130^\circ$  for about four hours. In almost all cases, however, the tubes burst during the heating, and when this was not the case they burst with great violence when the author attempted to open them, so that he was not able to obtain any of the product.

L. T. T.

**Ethyl Malonanilidate, Malonparatoluidic Acid, and Methyltrichloroquinoline.** By L. RUGHEIMER and R. HOFFMANN (*Ber.*, **17**, 739—741).—Potassium ethyl malonate is treated with phosphoric chloride dissolved in benzene, the mixture being heated to complete the reaction; after cooling, excess of aniline dissolved in benzene is added, and the whole allowed to stand 24 hours; the benzene solution is then separated, washed with hydrochloric acid and water to remove aniline, and allowed to evaporate spontaneously, when a crystalline mass of impure *ethyl malonanilidate*,  $NHPh.CO.CH_2.COOEt$ , is obtained. This after purification melts at  $38$ — $39^\circ$ , is readily soluble in alcohol, chloroform, and benzene, insoluble in water and light petroleum.

*Malonparatoluidic acid*,  $NH(C_6H_5).CO.CH_2.COOH$ , prepared from paratoluidine and malonic acid, crystallises in small colourless needles; melts with decomposition at  $156^\circ$ ; but on slowly heating, it softens and fuses at a still lower temperature. Heated with phosphorous pentachloride (comp. p. 1050) it yields *methyltrichloroquinoline*,  $C_9H_5MeCl_3N$ , crystallising in long needles, and melting at  $134^\circ$ .

A. J. G.

**Paranitrobenzoylacetic Acid.** By W. H. PERKIN, Jun., and G. BELLENOT (*Ber.*, **17**, 326—328).—Baeyer has lately shown (*Abstr.*,

1883, 337) that ethyl phenylpropiolate is converted into ethyl phenylacetate by simple solution in cold strong sulphuric acid. The authors find that a similar reaction takes place with ethyl paranitropropiolate, but the sulphuric acid solution requires to be heated to 35—40°. The cooled mixture is then poured on powdered ice, when paranitrobenzoyl acetic acid separates as a white amorphous mass.

*Paranitrobenzoyl acetic acid* crystallises from benzene in almost colourless needles, melting at 135°, and giving off carbonic anhydride at the same time. It is easily soluble in alcohol, ether, benzene, chloroform, and carbon bisulphide, sparingly so in light petroleum. Its alcoholic solution gives a violet coloration with ferric chloride, the shade being redder than that obtained with the non-nitrated acid. It forms unstable salts. The *ethyl salt* is obtained by saturating a solution of the acid in absolute alcohol with hydrochloric acid. The temperature must not be allowed to rise above 10°, or decomposition sets in, paranitracetophenone being formed. The ethereal salt crystallises in almost colourless needles, which melt at 49—50°, and are soluble in ether, alcohol, and benzene.

*Ethyl nitrosoparanitrobenzoyl acetate* is obtained by saturating a dry etheric solution of the nitro-acid with nitrous acid. It crystallises in needles melting at 220°, and soluble in alcohol, ether, and acetone.

L. T. T.

**Acetyl-derivatives of Aromatic Amidosulphonic Acids.** By R. NIETZKI and T. BENCKISER (*Ber.*, 17, 707—708).—Acetic anhydride has no action on sulphanilic acid, even when boiled with it; it reacts however readily with sodium sulphanilate at 140°, the liquid solidifying on cooling to a viscid colourless mass, from which, by dissolving in the least possible quantity of water, and adding alcohol and ether, small colourless prisms of *sodium acetylsulphanilate*,



are obtained. This salt is very soluble in water, moderately soluble in alcohol, nearly insoluble in ether. By heating with hydrochloric acid, it is decomposed into acetic and sulphanilic acids. The lead and barium salts were also prepared; on addition of alcohol to a solution of the latter, it is precipitated as a jelly which slowly becomes crystalline. The free acid could not be isolated.

In the cases of metamidobenzenesulphonic acid, of the sulphonic acids of paratoluidine and  $\alpha$ -naphthylamine, the free acids are not converted into acetyl-derivatives by acetic anhydride, although their salts are very readily acetylated; orthotoluidine-parasulphonic acid, on the contrary, is converted into an acetyl-derivative when heated with acetic anhydride.

A. J. G.

**Constitution of Phthalyl Chloride.** By E. NÖLTING and G. v. BECHI (*Ber.*, 17, 387—388).—The formation of phthalophenone by the action of phthalyl chloride on mercury phenyl is cited in support of the unsymmetrical formula  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{CCl}_2 \end{smallmatrix}\rangle\text{O}$  for phthalyl chloride.

W. C. W.



**Thiophthalic Anhydride.** By C. GRAEBE and B. ZSCHOKKE (*Ber.*, 17, 1175—1177).—Thiophthalic anhydride, described by Schreder (*Ber.*, 7, 705), may be more conveniently prepared by slowly adding phthalic chloride to a cold concentrated solution of sodium hydrogen sulphide. On acidifying the solution with hydrochloric acid, the thiophthalic anhydride is precipitated. This substance melts at  $114^{\circ}$ , and boils at  $284^{\circ}$ . It is converted into phthalimide and sulphuretted hydrogen by ammonia.

**Thiofluorescein** is formed by warming at  $40^{\circ}$  a mixture of the anhydride with resorcinol and strong sulphuric acid. The product is extracted with boiling water, dissolved in a solution of sodium carbonate and precipitated by hydrochloric acid. The precipitate is extracted with chloroform to remove thiophthalic acid. Thiofluorescein is soluble in alcohol and in wood spirit. It dissolves in alkalis, forming a red solution which exhibits a dark-green fluorescence. It can be distinguished from fluorescein by its absorption-spectrum. By treating the acetic acid solution with bromine, a *thioeosin* is obtained.

W. C. W.

**Hemlock Tannin.** By C. BÖTTINGER (*Ber.*, 17, 1041—1043).—The author has prepared this acid from American hemlock tannin extract. A solution of hemlock tannin is darker in colour than a solution of oak-bark tannin of equal strength. With alkalis, sulphuric acid, or hydrochloric acid, it behaves like oak-bark tannin, but the "hemlock-red" precipitated by hydrochloric acid is darker in colour than the corresponding "oak-red." Bromine precipitates from an aqueous solution of hemlock tannin a yellow substance, soluble in alcohol, ethyl acetate, acetone, and in warm acetic anhydride. It is insoluble in chloroform, carbon bisulphide, and water, but soluble in alkalis. The results of analysis lead to the formula  $C_{20}H_{14}Br_4O_{10}$ , and from this it follows that the original substance has the formula  $C_{20}H_{18}O_{10}$ , and that hemlock tannin is a homologue of oak-bark tannin,  $C_{19}H_{16}O_{10}$ . In presence of hydrochloric acid tetrabromo-tannin from hemlock behaves like dibromotannin from oak-bark. It forms with acetic anhydride a penta-acetyl-derivative, and when dissolved in chloroform can be further brominated, with formation of a hexabromide,  $C_{20}H_{10}Br_6O_{10}$ . The investigation of this tannin will be continued by the author.

A. B.

**Bark Tannins.** By C. BÖTTINGER (*Ber.*, 17, 1123—1131).—The precipitate which is produced on the addition of bromine to the cold aqueous extracts of tannin from different sources varies in colour and in composition. Tannin from oak-bark gives a brownish-yellow precipitate, containing 28.4 per cent. Br. The hemlock and quebracho precipitates are reddish-yellow, and contain from 42.1 to 44.5 per cent. Br, whilst the mimosa, chestnut, and terra japonica compounds are pale yellow, and contain from 49.3 to 53.2 per cent. Br.

A red compound,  $C_{40}H_{30}O_{17}$ , is formed when hemlock tannin is warmed with strong hydrochloric or sulphuric acid. It is purified by washing with water and extracting the dry mass with ether and with hot alcohol. This substance dissolves in cold soda-lye, and also in a warm solution of sodium carbonate. It is decomposed by strong

hydrochloric acid at  $180^{\circ}$ , yielding water, carbonic anhydride, methyl chloride, and a black compound. Hemlock-red forms an acetic derivative,  $C_{40}H_{23}\overline{AC}_7O_{17}$ , which is insoluble in water and ethyl acetate, but is decomposed by alcohol. By the action of bromine on hemlock-red suspended in chloroform, two crystalline bromo-derivatives are obtained, viz.,  $C_{40}H_{20}Br_{10}O_{17}$ , and  $C_{40}H_{20}Br_{14}O_{17}$ . The bromo-derivative of pine tannin,  $C_{21}H_{14}Br_6O_{10}$ , is very unstable. It is soluble in alcohol, ethyl acetate, and dilute alkalis. The acetic derivative,  $C_{21}H_5\overline{AC}_5Br_3O_{10}$ , is a yellow powder, soluble in acetone and ethyl acetate. The red compound produced by the action of hydrochloric acid on this tannin yields an acetic derivative of the composition  $C_{42}H_{27}\overline{AC}_7O_{17}$ , and a bromine-derivative,  $C_{42}H_{24}Br_{10}O_{17}$ ; but if sulphuric acid is used instead of hydrochloric, the acetic derivative has the composition  $C_{42}H_{26}\overline{AC}_6O_{16}$ . Tannin from *terra japonica* yields the derivatives,  $C_{21}H_{14}\overline{AC}_4O_9$  and  $C_{21}H_{14}\overline{AC}_3O_8$ . Oak-bark tannin appears to be a methyl salt of a condensation-product of tannin and acetoacetic aldehyde.

W. C. W.

**Formation of Indigo from Orthamidoacetophenone.** By A. BAEYER and F. BLOEM (*Ber.*, **17**, 963—970).—Formation of *acetylorthamidoacetophenone*. The starting point for the preparation of this substance is orthamidophenylacetylene (*Abstr.*, 1882, 623). On adding slowly 50 grams of the latter to a mixture of 200 c.c. of water and 600 c.c. concentrated sulphuric acid, the sulphate of the original base at first crystallises out, but afterwards dissolves, and the solution is then left until no phenylacetylene is to be found on testing with an ammoniacal solution of cuprous chloride. The solution is cooled with ice, neutralised with soda, and distilled in steam; the distillate is saturated with sodium chloride, and the orthamidoacetophenone extracted with ether; it is converted into the acetyl-derivative by boiling it with acetic anhydride.

By acting on acetylorthamidoacetophenone with bromine in aqueous or glacial acetic acid solution, a bromo-substitution-product is obtained, in which the hydrogen of the benzene-ring is replaced by bromine. If the action of bromine is direct, or in presence of concentrated sulphuric acid, hydrogen, chiefly in the side chain, is replaced; it is only from the latter that indigo is obtainable.

*Esobromoacetylorthamidoacetophenone*.—(For the new nomenclature of this and the following substances, see this vol., p. 998). This compound is formed from the acetic acid solution of the acetylorthocompound by the action of bromine. It forms slender colourless needles, melting at  $160^{\circ}$ , and soluble in hot alcohol, but nearly insoluble in cold. On oxidation by means of a warm alkaline solution of permanganate, it yields a red substance crystallising from alcohol, and melting at  $250^{\circ}$ ; it appears to be a monobromisatin. The bromine is therefore in the benzene-ring, the formula is  $COMe.C_6H_3Br.NH\overline{AC}$ , and it is the parabromo-compound in relation to the amido-group. It is therefore metabromorthacetyl-amidoacetophenone.

*ω-Dibromometabromorthacetyl-amidoacetophenone*,



By the action of bromine on acetylamidoacetophenone in a solution of chloroform, sulphuric acid, or carbon bisulphide, or directly on the dry substance, bromo-substitution compounds are formed, in which bromine replaces hydrogen both in the benzene-ring and in the side chain. In the case of chloroform, little in the side chain is replaced, and by direct action on the dry substance the side chain substitution is the greatest. The reaction is complete when two hydrogen-atoms in the side chain, and one in the benzene-ring, are replaced. If the reaction is incomplete, intermediate products are formed which are difficult to separate. The above tribromo-derivative has been investigated: it is best formed by acting on the acetyl-compound, in presence of a little iodine, with bromine-vapour for five days, the yield being a quantitative one. It is obtained as a yellowish powder, soluble in chloroform, but only sparingly in alcohol. It becomes brown at  $180^{\circ}$ , and melts at  $185^{\circ}$  with decomposition. By oxidation with permanganate, monobromisatin is obtained, and consequently the formula of the above compound may be established. By the action of hydrobromic acid, it loses the acetyl-group, giving  $\omega$ -dibromometabromorthamidoacetophenone,  $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}\cdot\text{CHBr}_2$ , as orange-yellow needles, melting with decomposition at  $140\text{--}145^{\circ}$ , readily soluble in alcohol and ether, but sparingly in water. On heating it with acetic anhydride, the original acetyl-compound is again obtained.

*$\omega$ -Dichlorometabromorthamidoacetophenone*,  $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}\cdot\text{CHCl}_2$ , is obtained by boiling the tribromacetyl-compound with concentrated hydrochloric acid, until it is dissolved. From this solution fine orange-yellow needles separate; they are soluble in alcohol, melt at  $110\text{--}120^{\circ}$ , and sublime with little decomposition at a higher temperature.

*Formation of Indigo from Exobromo- and Exochloro-orthamidoacetophenones and their Derivatives.*— $\omega$ -Dibromometabromorthamidoacetophenone when boiled with dilute soda solution dissolves with a brownish-yellow colour, and on cooling the solution and agitating it with air bromindigo separates. It is readily distinguished from indigo by its solubility in chloroform. By similar treatment, the less brominated substitution-products of this acetyl-compound yield either indigo or a mixture of indigo and bromindigo. The corresponding compounds which do not contain the acetyl-group behave in the same way. On acidifying the solution of the tribromo-compound in soda, after the separation of the bromindigo, bromisatin may be extracted with ether. On acidifying, however, the solution of the tribromo-compound previous to oxidation, bromindirubin is precipitated. These reactions are easily explained on the assumption that by boiling the tribromo-compound with soda, sodium isatate and indoxyl (or at any rate their bromo-substitution-compounds) are formed in the solution; bromindigo is then produced from the bromindoxyl by the action of air, but if acid be previously added, the bromisatin formed (Abstr., 1884, 76) acts on the bromindoxyl, yielding bromindirubin. The simultaneous formation of bromisatin and bromindoxyl is easily understood, since, owing to the presence of the two bromine-atoms in the side chain, compounds of an aldehydic nature may be formed, and these in alkaline solutions allow

of the formation of an acid (isatic acid) and an alcohol which by loss of water yields indoxyl.

*ω*-Dichlorometabromo-orthamidoacetophenone behaves precisely similarly to the corresponding bromo-compound. A. B.

**Chlorobenzaldehyde and Chlorindigo.** By R. GNEHM (*Ber.*, **17**, 752—755).—One of the chief obstacles to the commercial success of the manufacture of artificial indigo lies in the small yield of ortho-nitrobenzaldehyde obtained by nitration of benzaldehyde, the main product being the meta-compound. It seemed probable that a more favourable yield of the orthonitro-compound might be obtained by nitrating some chloro-substitution derivative of benzaldehyde in which the ortho-position was still unoccupied, and that the chlorindigo finally obtained might be sufficiently like indigo to be used in dyeing. *Dichlorobenzaldehyde*,  $C_7H_4Cl_2O$  (the method of preparation is not given), crystallises in snow-white crystals, melts at 57—58° (uncorr.), and boils at 230—233°. On oxidation, it yields a dichlorobenzoic acid melting at 152°, which by treatment with nitric and sulphuric acids is converted into *orthonitro-dichlorobenzaldehyde*, crystallising in nacreous plates or needles. These melt at 136—138°, and are converted into chlorindigo by treatment with acetone and caustic soda.

*Tetrachlorindigo*,  $C_{16}H_6Cl_4N_2O_2$ , closely resembles indigo in appearance; when heated it gives off violet vapours and condenses in blue needles of coppery lustre. Treated with reducing agents, it yields a tetrachlorindigo-white. The formation of an indigo vat with it is, however, attended with considerable difficulties, as it is less easily reduced than ordinary indigo, and the white is much less soluble in alkaline liquids than indigo-white. The difficulties have been so far overcome however, that satisfactory vat dyeing has been effected with it. The preparation of carmine from it is not satisfactory, as it requires more Nordhausen sulphuric acid and a higher temperature than ordinary indigo; moreover, the colours dyed with it are not equal to those obtained with indigo. A mixed di- and tetra-chlorindigo prepared from a mixture of dichloro- with monometa-chlorobenzaldehyde showed similar properties.

*Amido-dichlorobenzaldehyde*,  $C_7H_3Cl_2O.NH_2$ , prepared by reducing the nitro-compound with ferrous sulphate and ammonia, crystallises in yellow needles, which melt at 77—78°: it is sparingly soluble in water, soluble in hydrogen sodium sulphite. When heated with acetone and caustic soda, it yields dichloroquinaldine as a yellowish solid melting at 46°, boiling at 300°, soluble in mineral acids; the picrate crystallises in fine needles. Amidodichlorobenzaldehyde when heated with phenylhydrazine yields a compound which crystallises in yellow needles, melting at 200°. A. J. G.

**Indirubin.** By C. FORRER (*Ber.*, **17**, 975—982).—The author has continued the investigation of this substance which was first obtained by Baeyer (*Ber.*, **14**, 1745) by the action of isatin on indoxyl. Indirubin is best obtained by boiling one part of ethylic indoxylate in

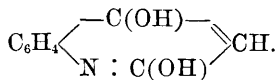
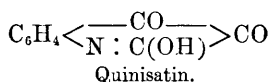
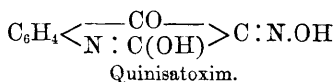
100 parts of water (to convert it into indoxyl), filtering off any indigo or resinous matters which may be formed, and then boiling this solution with  $\frac{3}{4}$  part isatin in 200 parts of water. On filtering and adding soda solution, indirubin separates out as a flocculent mass; when dried it is a light red-brown powder, with a green metallic lustre. It is somewhat soluble in alcohol and similar solvents with a purple-violet colour; in acetic acid and acetic anhydride, it is more soluble. Sulphuric acid converts it into a sulphonic acid.

Indirubin like indigo yields isatin on oxidation. On reduction with zinc and soda solution, it also behaves like indigo (*Ber.*, 1, 17). On reduction with zinc and acetic acid, hydroindirubin is at first formed, and this on exposure to the air in presence of alkalis is again converted into indirubin; on prolonging the reducing reaction, however, a crystalline product is obtained which remains colourless when exposed to air. The author proposes to call this *indileucin*; the results of analysis are between the formulæ  $C_{15}H_{12}N_2O$  and  $C_{16}H_{14}N_2O$ , but from subsequent reactions the former seems to be the more likely. Indileucin crystallises from alcohol in colourless needles which at  $220^\circ$  become brown, and at  $260^\circ$  are completely decomposed. It is sparingly soluble in ether, alcohol, chloroform, and benzene, but easily in acetone and glacial acetic acid. It forms crystalline compounds with bromine and picric acid. A methyl-compound,  $C_{16}H_{11}MeN_2O$ , and an acetyl-compound,  $C_{16}H_9N_2OAc_3$ , have also been prepared. A. B.

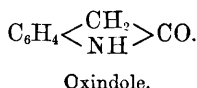
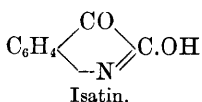
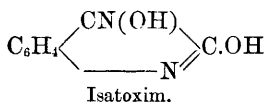
**Quinisatin.** By A. BAEYER and B. HOMOLKA (*Ber.*, 17, 985—987). In the authors' first paper (this vol., 78) it was left undecided whether by the union of the  $\omega$  or  $\alpha$  carbon-atoms with the nitrogen of quinisatinic acid, quinisatin was formed, that is, whether quinisatin is a lactam or a lactim (Abstr., 1883, 202). The study of the action of hydroxylamine on quinisatin shows that it is probably the  $\omega$ -lactim of quinisatinic acid. (For this nomenclature see p. 998.)

Quinisatoxim is easily formed by the action of hydroxylamine chloride on quinisatin, it crystallises from alcohol in orange prisms melting at  $208^\circ$ , and is identical with the previously described nitroso- $\gamma$ -hydroxycarbostyryl (Abstr., 1883, 202).

Quinisatoxim stands in the same relation to Py-[1·3]-dihydroxyquinoline ( $\gamma$ -hydroxycarbostyryl) and to quinisatin as isatoxim does to oxindole and isatin.



Py (1·3) Dihydroxyquinoline.



A. B.

**Indole.** By A. LIPP (*Ber.*, **17**, 1067—1073).—In the first part of this paper an account is given of the various researches on indole and on the means used to obtain proof of its constitutional formula.

Baeyer has given it the constitutional formula  $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{CH} \end{array} \text{CH}$ , on

the ground that it contains an imide-group. It may thus be considered as an internal anhydride derived from an hypothetical orthamidophenyl vinyl alcohol or from its ether,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{OC}_2\text{H}_5$ . This substance has never been prepared, owing to the difficulty of nitrating phenyl vinyl ether without decomposition. The author has however, succeeded in preparing orthonitrochlorostyrolene, in reducing it to the amido-derivative, and from the latter obtaining indole, probably by the intermediate formation of orthonitrophenyl vinyl ether.

*Orthonitrochlorostyrolene*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CHCl}$ , is obtained as a bye-product in the formation of orthonitrophenylchlorolactic acid, (just as chlorostyrolene is obtained in the formation of phenylchlorolactic acid) by the action of hypochlorous acid on sodium orthonitrocinnamate, and subsequent treatment with soda (*Abstr.*, 1882, 191). It crystallises from alcohol in bright yellow needles or prisms, insoluble in cold but slightly soluble in hot water, and readily soluble in hot alcohol and ether. It melts at  $58^\circ$ , but decomposes at a higher temperature. Warm concentrated hydrochloric acid and tin reduce it to the hydrochloride of orthamidochlorostyrolene, from which the free base may be obtained by the action of potash.

*Orthamidochlorostyrolene*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CHCl}$ , is readily soluble in alcohol and ether, very sparingly in water, and crystallises from ether in white prisms. On heating it with sodium alcoholate in a sealed tube at  $160$ — $170^\circ$  for three or four hours, sodium chloride is formed, and, on opening the tube, the presence of indole may be recognised by its powerful odour, and by its reactions. On adding water to the contents of the tube, indole separates out as an oil, and may be purified by distillation in steam, and crystallisation from hot water. The indole thus obtained melts at  $52^\circ$ , and agrees in all its properties with that prepared from indigo or albumin. A. B.

**Occurrence of Diphenyl in Coal-tar Oil.** By K. E. SCHULZE (*Ber.*, **17**, 1203—1204).—The presence of diphenyl in tar oil may be proved by removing phenols and amines from the portion boiling between  $200^\circ$  and  $300^\circ$ ; the mono- and di-methylnaphthalenes are then converted into sulphonic acids by treatment with warm sulphuric acid, and on cooling the undissolved oil, to  $-15^\circ$ , diphenyl crystallises out. W. C. W.

**Reactions of Triphenylmethyl Bromide.** By K. ELBS (*Ber.*, **17**, 700—701).—Triphenylmethyl thiocyanate prepared by mixing solutions of ammonium thiocyanate and triphenylmethyl bromide, crystallises in lustrous reddish-white prisms, melts at  $137^\circ$ , can be distilled, is sparingly soluble in alcohol and ether, readily soluble in chloroform.

By acting on triphenylmethyl bromide with potassium sulphide, a crystalline sulphur-compound is obtained.

By the action of potassium cyanide, the bromide is converted into the triphenylacetone nitrile of E. and O. Fischer (Abstr., 1879, 385). This, by reduction with zinc and hydrochloric acid, is converted into *triphenylethylamine hydrochloride*, a substance crystallising in needles which melt at 247°, and are very readily soluble in alcohol, but almost insoluble in water. The platinochloride crystallises from alcohol in large orange-red needles. *Triphenylethylamine* is crystalline, melts at 116°, dissolves sparingly in cold alcohol, readily in ether. It is very much more stable than the corresponding triphenylmethylamine.

Triphenylmethyl bromide when dissolved in benzene and boiled with sodium is only very slightly attacked. Fused with magnesium powder, it yields phenylenediphenylmethane; with powdered copper a mixture of crystalline compounds is formed. Aluminium chloride, when heated with a solution of the bromide in benzene converts it into triphenyl carbinol and a yellow resin.

A. J. G.

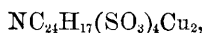
**Amido-derivatives of Triphenylmethane.** By K. ELBS (*Ber.*, 17, 701—706).—A continuation of the author's researches on this subject (comp. Abstr., 1883, 1000; also Nauen, this vol., 849, and Hemilian and Silberstein, next Abstract). *Triphenylamidomethane platinochloride* is very unstable, being partly decomposed into triphenyl carbinol and ammonium platinochloride by drying or by treatment with excess of water. The hydrochloride is nearly as unstable, its aqueous solution being decomposed by boiling into ammonium chloride and triphenyl carbinol. The *oxalate* forms hard colourless granular crystals, melts at 253°, and is very sparingly soluble in alcohol. Triphenylamidomethane is most conveniently prepared by treating a solution of triphenylmethyl bromide for half an hour with a stream of dry ammonia gas and then with a current of steam, when the benzene distils, ammonium bromide dissolves in the water, and the free amine remains behind as a yellowish oil, which solidifies on cooling, and is obtained pure by a single crystallisation from ether. Triphenyl carbinol is readily obtained from triphenylamidomethane hydrochloride by treatment with potassium nitrite, or from the free amine by solution in nitric acid (sp. gr. 1.5), or concentrated sulphuric acid and subsequent addition of water, when a white precipitate of the pure carbinol is obtained. *Triphenylmethyl-benzylamine hydrochloride*, obtained by the action of benzyl chloride on triphenylamidomethane, crystallises in colourless needles, melts at 249°, is sparingly soluble in water, readily in alcohol. The free base crystallises in prisms, melts at 110°, and is readily soluble in alcohol and ether.

*Triphenylmethyl-aniline*,  $\text{NHPH.CPh}_3$ , is prepared by the action of an excess of aniline on a solution of triphenylmethyl bromide in benzene. It crystallises in colourless prisms, melts at 146°, is sparingly soluble in alcohol, soluble in ether, very readily soluble in benzene. The salts of this base are still more unstable than those of triphenylamidomethane; in most cases only aniline salts could be isolated.

*Nitrosotriphenylmethyl-aniline*, obtained by the action of excess of

amyl nitrite on an ethereal solution of the amine, crystallises in nearly colourless concentrically grouped prisms. By very careful heating, it can be melted at about  $156^{\circ}$ ; but if heated more quickly it explodes at  $150^{\circ}$ . It is but little soluble in benzene, carbon bisulphide, or alcohol, insoluble in ether. When its benzene solution is mixed with platinum chloride, it yields diazobenzene platinumchloride and triphenyl carbinol. By the action of zinc chloride on a solution of the nitroso-compound, and subsequent treatment with potash, a base is obtained in the form of a dark blue powder; its hydrochloride crystallises in needles having a metallic green lustre, and the platinumchloride forms a reddish-black powder.

Nordhausen sulphuric acid converts triphenylmethyl-aniline into a sulphonic acid; the barium salt,  $\text{NH}(\text{C}_6\text{H}_4.\text{SO}_3).\text{C}(\text{C}_6\text{H}_4.\text{SO}_3)_3\text{Ba}_2$ , forms a white crystalline precipitate, the copper salt,



a moss-green cauliflower-like mass. By treatment with sodium nitrite and acetic acid, the barium salt is converted into barium sulphate, and a crystalline sodium salt, which is very readily soluble in water, and explodes on heating.

**TRIPHENYLMETHYL-TOLUIDINES.** By O. WITTICH. *Triphenylmethyl-orthotoluidine*,  $\text{NH}(\text{C}_6\text{H}_4\text{Me}).\text{CPh}_3$ , prepared in a similar manner to the aniline compound, forms lustrous prisms, and melts at  $142^{\circ}$ .

*Triphenylmethyl-paratoluidine*,  $\text{NH}(\text{C}_6\text{H}_4\text{Me}).\text{CPh}_3$ , forms fine crystals having numerous faces, and melts at  $177^{\circ}$ . *Nitrosotriphenylmethyl-paratoluidine*,  $\text{N}(\text{C}_6\text{H}_4\text{Me})(\text{CPh}_3)\text{NO}$ , obtained by the action of an excess of amyl nitrate on an ethereal solution of the base, crystallises in large yellowish prisms, melts at  $145\text{--}148^{\circ}$ , but does not explode on heating, and is sparingly soluble or insoluble in the ordinary solvents. Great difficulty was found in preparing salts of the triphenylmethyl-toluidines, on account of their ready decomposition into triphenyl carbinol and toluidine salts.

A. J. G.

**Triphenylamidomethane.** By W. HEMILIAN and H. SILBERSTEIN (*Ber.*, **17**, 741—752; comp. Elbs, *Abstr.*, 1883, 1000; and this vol., p. 1031).—*Triphenylamidomethane*,  $\text{NH}_2.\text{CPh}_3$ , prepared by the action of dry ammonia gas on a solution of triphenylmethyl bromide in benzene, crystallises in colourless needles, melts at  $103^{\circ}$ , and cannot be distilled without decomposition. It is insoluble in water, moderately soluble in cold alcohol, readily soluble in carbon bisulphide, chloroform, benzene, and ether. All the salts crystallise with water of crystallisation, have a bitter taste, are readily soluble in alcohol, very sparingly soluble in water, and are precipitated by addition of water to the alcoholic solutions. They are all readily decomposed by water on gentle heating, being converted into ammonium salts and triphenyl carbinol. Alcoholic solutions of the salts are not decomposed by nitrous acid in the cold; but if heated with potassium nitrite, they readily yield triphenyl carbinol. The *hydrochloride*,  $\text{NH}_2.\text{CPh}_3.\text{HCl}$  + aq., crystallises in colourless prisms; the *platinochloride*,  $(\text{NH}_2.\text{CPh}_3)_2.\text{H}_2\text{PtCl}_6 + 7\frac{1}{2}\text{H}_2\text{O}$ , forms golden-yellow plates;



it slowly loses its water of crystallisation over sulphuric acid, completely at  $110^{\circ}$  (comp. Elbs, *loc. cit.*). The nitrate forms satiny-white plates, and explodes when heated; the sulphate crystallises from alcohol in nodules. A carbamide derivative could not be obtained.

*Acetotriphenylmethylamine*,  $\text{NHAc.CPh}_3$ , prepared by heating triphenylamidomethane very gently on the water-bath with acetic chloride or anhydride, forms slender colourless needles, melts at  $207-208^{\circ}$ , is readily soluble in ether and chloroform, less soluble in alcohol. At  $100^{\circ}$ , acetic chloride decomposes triphenylamidomethane into triphenyl carbinol, &c. Attempts to prepare the secondary amine,  $\text{NH(CPh}_3)_2$ , were unsuccessful. By the action of methyl iodide on triphenylamidomethane, an indistinctly crystalline white mass is obtained, from which alkalis liberate a mixture of bases, whose separation could not be effected.

*Methyl-triphenylmethyl-amine*,  $\text{NHMe.CPh}_3$ , prepared by the action of dry dimethylamine gas on a hot solution of triphenylmethyl bromide in benzene, crystallises in aggregates of colourless prisms, melts at  $73^{\circ}$ , very readily exhibits superfusion, is soluble in alcohol, benzene, and light petroleum, insoluble in water. The hydrochloride is obtained as a white crystalline precipitate on saturating a solution of the base in benzene with hydrochloric acid. It is readily soluble in alcohol, very sparingly soluble in water. When boiled with water, it is decomposed into triphenyl carbinol and methylammonium chloride. The *platinochloride*,  $(\text{NHMe.CPh}_3)_2.\text{H}_2\text{PtCl}_6 + 6\text{H}_2\text{O}$ , crystallises in yellow prisms; the water of crystallisation is only partly expelled by continued heating at  $110^{\circ}$ .

*Dimethyl-triphenylmethyl-amine*,  $\text{NMe}_2.\text{CPh}_3$ , prepared by the action of dimethylamine on triphenylmethyl bromide dissolved in benzene, crystallises in aggregates of colourless crystals resembling those of ammonium chloride; it melts at  $97^{\circ}$ , and is readily soluble in the ordinary solvents with the exception of water. The hydrochloride is obtained as a white crystalline precipitate. The *platinochloride*,  $(\text{NMe}_2.\text{CPh}_3)_2.\text{H}_2\text{PtCl}_6$ , is obtained as an anhydrous crystalline yellow precipitate.

*Triphenylmethyl-aniline*,  $\text{NHPh.CPh}_3$  (comp. K. Elbs., *loc. cit.*), prepared by the action of triphenylmethyl bromide on aniline, both in solution in benzene, crystallises in slender colourless prisms, melts at  $144.5^{\circ}$ , is very sparingly soluble in alcohol, more soluble in ether and light petroleum, readily soluble in carbon bisulphide and chloroform. Concentrated acids decompose it, even in the cold, into triphenyl carbinol and an aniline salt.

*Action of the Halogens on Triphenylamidomethane.*—With this substance and its methyl-derivatives, iodine and, although less readily, bromine, give additive products, whilst chlorine causes their decomposition into triphenyl carbinol and ammonium chloride.

By the action of iodine on triphenylamidomethane, both in solution in carbon bisulphide, a brown liquid is formed, from which, after standing, well-formed crystals of two additive compounds are deposited, and can be separated mechanically. The compound



forms large transparent dark-red prisms, sparingly soluble in chloroform, more readily in carbon bisulphide, nearly insoluble in light petroleum, very readily soluble with decomposition in alcohol. By agitation with mercury or silver, all iodine is removed, and the free base obtained. These red crystals are formed exclusively if chloroform is used in place of carbon bisulphide as the solvent. The other compound,  $(\text{NH}_2.\text{CPh}_3)_2\text{I}_2$ , forms black opaque prisms of copper-red metallic lustre; it loses iodine on exposure to air. It is readily soluble in warm carbon bisulphide, insoluble in light petroleum, and is decomposed by alcohol.

Only a single bromine-compound was obtained. It forms dark yellow to red crystals, of the formula  $\text{NH}_2(\text{CPh}_3)\text{Br}_2$ , sparingly soluble in carbon bisulphide, insoluble in light petroleum; it is decomposed by heating with alcohol or benzene.

The iodine-compound of methyl-triphenylmethyl-amine crystallises in bluish-black needles of metallic lustre. It has the formula  $(\text{NHMe}.\text{CPh}_3)_2\text{I}_2$ . The iodine-compound of dimethyl-triphenylmethyl-amine forms very small greyish-black needles. It was too unstable to obtain satisfactory analytical results. Bromine-compounds of these methylated bases and of the corresponding phenylated base could not be obtained.

A. J. G.

**Chrysaniline.** By R. ANSCHÜTZ (*Ber.*, **17**, 433—437).—*Diacetylchrysaniline*,  $\text{C}_{19}\text{H}_{13}\text{N}_3\text{Ac}_2$ , is prepared by heating a mixture of crude chrysaniline and acetic anhydride at  $140^\circ$  in sealed tubes. The crude product is poured into water, and the resinous precipitate is extracted with boiling water. On adding hydrochloric acid to this solution, the hydrochloride is deposited. If this salt is dissolved in soda-lye and the solution poured into water, diacetylchrysaniline is precipitated; it dissolves in alcohol, forming a blue fluorescent solution, but it is insoluble in water. The *hydrochloride*,  $\text{C}_{19}\text{H}_{13}\text{N}_3\text{Ac}_2.\text{HCl}$ , is obtained in yellow needle-shaped crystals when hydrochloric acid is added to a solution of the base in acetic acid. It is soluble in hot water, and the solution dyes wool and silk yellow. When silver nitrate is added to a solution of this salt, a mixture of silver chloride and diacetylchrysaniline nitrate is precipitated, from which the latter is extracted by boiling water. Pure chrysaniline is best prepared by boiling the acetyl-derivative with hydrochloric acid for several hours. The liquid is evaporated to dryness, and the residue dissolved in water. The addition of nitric acid precipitates the nitrate, from which the chrysaniline is liberated by precipitation with soda: by recrystallisation from dilute alcohol, it may be obtained in prismatic needles.

Chrysaniline is oxidised by chromic mixture with formation of acridine, of a base which melts at  $148^\circ$ , and a third base which is probably amidoacridine.

W. C. W.

**Tetraphenylethane.** By R. ANSCHÜTZ and J. KLEIN (*Ber.*, **17**, 1039—1041).—In a previous communication (this vol., 326), it has been stated by Anschütz that tetraphenylethane obtained from unsymmetrical tetrabromethane or from  $\beta$ -benzopinacoline is unsym-

metrical, and that tetraphenylethane obtained from stilbene bromide, which should be symmetrical from its formation, is identical with the unsymmetrical form, and that probably an intermolecular change takes place in the stilbene bromide. It had also been found that whilst acetylidene tetrabromide and benzene in presence of aluminium chloride yielded tetraphenylethane, acetylene tetrabromide yielded anthracene, and on this ground the unsymmetrical character of tetraphenylethane was based. Anschütz and Eltzbacher have, however, since found that tetraphenylethane is also obtained from acetylene tetrabromide along with anthracene. This has caused the authors to doubt the correctness of the constitutional formula of tetraphenylethane. They have found that the tetraphenylethanes prepared in eleven different ways seem to be always identical, as shown by the measurements of the crystalline compound formed with benzene. They are therefore inclined to consider that tetraphenylethane prepared in these eleven ways is symmetrical, since out of the eleven only two methods point directly to the formation of the unsymmetrical. Its formation by the reduction of tetraphenylethylene,  $\text{CPh}_2 : \text{CPh}_2$ , which can only have a symmetrical formula, also points to the likelihood of the compound being symmetrical. A. B.

**$\beta$ -Ethyl-naphthalene.** By O. BRUNEL (*Ber.*, **17**, 1179—1180).— $\beta$ -Ethyl-naphthalene can be prepared by adding the requisite amount of ethyl bromide in successive portions to  $\beta$ -bromonaphthalene and sodium, and heating the mixture at  $60^\circ$ .  $\beta$ -Ethyl-naphthalene boils at  $250^\circ$  and solidifies at  $-19^\circ$ , at which temperature  $\alpha$ -ethyl-naphthalene remains liquid. The picric acid compound melts at  $69^\circ$ .  $\beta$ -Ethyl-naphthalene is also formed by treating ethyl bromide and naphthalene with aluminium chloride.  $\beta$ -Methylnaphthalene could not be prepared by either of these methods. W. C. W.

**Action of Ammonia on Nitroso- $\beta$ -naphthol.** By M. ILINSKI (*Ber.*, **17**, 391—393).—Nitroso- $\beta$ -naphthol is converted into *nitroso-amidonaphthalene*,  $\text{C}_{10}\text{H}_6(\text{NO})\cdot\text{NH}_2$ , by the action of ammonia at  $100^\circ$ . This base is much more soluble in hot solvents than in cold, and it is decomposed by alkalis and reconverted into nitroso-naphthol. It crystallises in dark green prismatic needles, which melt at  $151^\circ$ .  $\beta$ -nitroso- $\alpha$ -naphthol behaves in a similar manner.

The nitroso-naphthols are decomposed by alcoholic potash at  $100^\circ$ , with formation of amorphous salts and evolution of ammonia.

W. C. W.

**Dinitro- $\beta$ -naphthol.** By C. GRAEBE and A. DREW (*Ber.*, **17**, 1170—1172).—The dinitronaphthol which Wichelhaus and Wallach obtained by nitrating  $\beta$ -naphthol, can be more easily prepared from  $\beta$ -naphthylamine. 100 grams of strong sulphuric acid diluted with a litre of water are added to a solution of 50 grams of  $\beta$ -naphthylamine in a litre of water containing 35 c.c. of hydrochloric acid (sp gr. 1.19). The mixture is then diluted until it occupies 3 litres. A solution containing 25 grams of sodium nitrite is next added to the cold liquid, which soon loses its turbidity. On boiling the mixture

with 400 c.c. of nitric acid (sp. gr. 1.35), nitrogen escapes and dinitronaphthol melting at  $194^{\circ}$  separates out. The potassium and sodium salts crystallise in yellow needles containing 2 mols.  $H_2O$ . They dye wool yellow. The silver salt,  $C_{10}H_5(NO_2)_2OAg$ , is sparingly soluble.

On oxidation with nitric acid or potassium permanganate, dinitro- $\beta$ -naphthol yields  $\beta$ -nitrophthalic acid (1 : 2 : 4). The ethylic salt of  $\beta$ -dinitronaphthol forms pale-yellow needle-shaped crystals melting at  $138^{\circ}$ , soluble in alcohol. It is converted into dinitro- $\beta$ -naphthylamine melting at  $238^{\circ}$ , by treatment with ammonia at  $140^{\circ}$ . Dinitronaphthalene can be obtained from this compound by adding sodium nitrite to its solution in dilute sulphuric acid. The dinitronaphthalene crystallises in pale-yellow needles which melt at  $161.5^{\circ}$ , and are soluble in alcohol.

W. C. W.

**Action of Ammonia on the Ethers of Nitronaphthol.** By L. WITTKAMPF (*Ber.*, **17**, 393—395).—The ethylic salt of mononitro- $\beta$ -naphthol, which is prepared by the action of nitric acid (sp. gr. 1.43) on ethyl- $\beta$ -naphthol dissolved in glacial acetic acid, crystallises in pale-yellow needles which melt at  $104^{\circ}$ ; it is soluble in hot alcohol or hot acetic acid. The compound is decomposed by alcoholic ammonia at  $170^{\circ}$ , yielding nitronaphthylamine melting at  $127^{\circ}$ , apparently identical with the substance Jacobson (*Ber.*, **14**, 1791) obtained from nitro- $\beta$ -acetonaphthalide.

W. C. W.

**Azo-colours.** By G. SCHULTZ (*Ber.*, **17**, 461—462).— $\beta$ -Naphthol- $\alpha$ -monosulphonic acid will only unite with diazo-xylene to form xylene-azo- $\beta$ -naphtholsulphonic acid when very concentrated solutions are employed.

A red colouring matter is formed by the action of tetrazodiphenyl (1 mol.) on an alkaline solution (1 mol.) of  $\beta$ -naphtholdisulphonic acid; it yields a sodium salt insoluble in alcohol. At the ordinary temperature, a similar result is obtained even if 2 mols. of the naphtholsulphonic are used, but if the mixture is warmed a blue substance is produced which is precipitated on the addition of common salt. The blue substance is soluble in water, and is turned red by alkalis. On adding acids to the alkaline solution, a purple precipitate is thrown down which turns blue when heated.

W. C. W.

**Azo-colours.** By R. NIETZKI (*Ber.*, **17**, 1350—1352).—The author a short time ago (this vol., p. 1016) described a blue colouring matter obtained by the action of an alkaline solution of  $\beta$ -dinaphtholdisulphonic acid on the diazo-compound of his red azo-colouring matter,  $NH_2.C_6H_4.N_2.C_{10}H_7(SO_3H)_2.OH$ , and ascribed to it the formula  $C_6H_4[N_2.C_{10}H_7(SO_3H)_2.OH]_2$ . Liebermann and v. Kostanecki (*Ber.*, **17**, 878) dispute the existence of this compound, contending that it is formed if alkali alone be added to the diazotised red azo-colouring matter without any addition of  $\beta$ -naphtholdisulphonic acid. The author now shows that the blue coloration alluded to by Liebermann and Kostanecki is only of an evanescent character, and that no blue colouring matter can be obtained from it; but that after the action of

naphtholdisulphonic acid the blue colouring matter described by him may be easily isolated. He further disproves Liebermann and Kostanecki's theory by substituting resorcinol and phenol for the naphtholdisulphonic acid. With resorcinol a reddish-violet, with phenol a magenta-red colouring matter is obtained; whereas if Liebermann and Kostanecki's view were correct, the same blue coloration must have been obtained in all cases. This blue colouring matter, in an acid bath, dyes wool and silk indigo-blue, but the colour is not permanent when exposed to the light.

L. T. T.

**Bromine Derivatives from Amidonaphthaquinonimide. I.** By E. KRONFELD (*Ber.*, **17**, 715—721).—By the action of bromine on amidonaphthaquinonimide, a mixture of substances is obtained from which the two principal products have been isolated and separated by means of the difference of their solubilities in chloroform. These stand, however, in no simple relation to the parent substance.

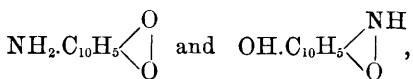
The substance insoluble in chloroform has the formula  $C_{10}H_6Br_3NO_3$ , crystallises from alcohol in compact lustrous crystals, from hot toluene in slender white lustrous needles; it melts at  $213^\circ$ , but at  $209^\circ$  the odour of bromine is marked. It has acid properties; when heated with water at  $100^\circ$ , it readily decomposes into phthalimide and bromoform, and at higher temperatures yields bromoform, phthalic acid, ammonia, and hydrobromic acid; the formation of formic acid was suspected but not proved. Alkalis in the cold decompose it into bromoform and phthalimide. It may be represented by the constitu-

tional formula  $C_6H_4 \begin{smallmatrix} \text{CO.CBr}_3 \\ \text{C(NH).COOH} \end{smallmatrix}$ . By heating the tribromide for some time at the melting point, or better, by heating it with sulphuric acid at  $140^\circ$ , a substance is obtained crystallising in long slender pale-yellow needles of the formula  $C_{18}H_{12}Br_4N_2O_2$ , and melting at  $237^\circ$ , soluble in glacial acetic acid and hot alcohol, insoluble in water.

The substance soluble in chloroform crystallises in white plates, melts at  $173^\circ$ , is readily soluble in benzene and chloroform, and has the formula  $C_9H_4Br_2O_2$ .

A. J. G.

**Hydroxynaphthaquinonimide (Oximidonaphthol) and Amidonaphthaquinonimide (Diimidonaphthol).** By E. KRONFELD (*Ber.*, **17**, 713—714).—Of the two formulæ,



proposed for oximidonaphthol, the author considers the second to best agree with the similarity of its behaviour to that of  $\beta$ -naphthaquinonanilide,  $OH.C_{10}H_5(NPh)O$ . On adding an equivalent quantity of sodium ethylate to an alcoholic solution of oximidonaphthol, the sodium salt separates in yellow needles. An aqueous solution of this salt gives red indistinctly crystalline precipitates with calcium and barium chlorides, and with silver nitrate a voluminous dark-red precipitate of the silver salt,  $OAg.C_{10}H_5(NH)O$ . Neither an ethyl nor an acetyl derivative could be obtained. On boiling the calcium or

barium salts with water, ammonia and hydroxynaphthaquinone are formed.

When *amidonaphthaquinonimide* is heated in glacial acetic acid solution with toluidine, it is converted into the compound



This forms red crystals, melts at  $178^\circ$ , is readily soluble in benzene and toluene, insoluble in ether. It readily yields salts which closely resemble those of the corresponding aniline-derivative.

A. J. G.

**Action of Aniline and Toluidine on Nitro- $\beta$ -naphthaquinone.**

By F. BRAUNS (*Ber.*, **17**, 1133—1136).—*Nitro- $\beta$ -naphthaquinonanilide*,  $\text{NO}_2.\text{C}_{10}\text{H}_7(\text{OH})(\text{NPh})\text{O}$ , is deposited as a reddish-green crystalline mass when 1 part of aniline is added to a solution of 1 part of nitro- $\beta$ -naphthaquinone in 10 of hot alcohol. The mother-liquor deposits yellow crystals of the composition  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4$ . Large quantities of this substance are formed when an excess of aniline is used and the mixture boiled.

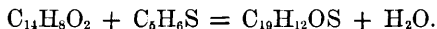
Nitronaphthaquinonanilide, melting at  $247^\circ$ , can be recrystallised from acetic anhydride. It acts as a strong acid, forming insoluble salts of calcium, barium, mercury, copper, and silver. It dissolves in solutions of alkalis and alkaline carbonates. The yellow aniline compound crystallises in needles melting at  $186^\circ$ , soluble in alcohol, benzene, and potash, but not in ammonia. It is also formed by the action of aniline on the red anilide suspended in benzene.

The bromine-derivative produced by treating nitro- $\beta$ -naphthaquinone with parabromaniline forms red crystals which melt at  $246^\circ$ . By boiling with alcohol and aniline, it is converted into the yellow bromine-free compound melting at  $186^\circ$ .

Ortho- and para-toluidine also act on nitro- $\beta$ -naphthaquinone, yielding a red orthotoluidine-derivative melting at  $240^\circ$ , and a yellow substance melting at  $144^\circ$ , whilst the corresponding para-compounds melt at  $241^\circ$  and  $222^\circ$  respectively. Aniline converts the nitro- $\beta$ -naphtha-quinotoluidines into toluides. The orthotoluide melts at  $154^\circ$  and the paratoluide at  $155^\circ$ .

W. C. W.

**Laubenheimer's Reaction.** By E. ODERNHEIMER (*Ber.*, **17**, 1338—1341).—V. Meyer showed (*Abstr.*, 1883, 1092) that Laubenheimer's colour reaction for phenanthraquinone (*Ber.*, **8**, 224) was due to the presence of thiotolene (methylthiophene) in the coal-tar toluene used. The author has now investigated the colouring matter formed. 1 gram phenanthraquinone is dissolved in 160 grams glacial acetic acid, 3.5 grams of a toluene containing 15 per cent. of thiotolene (methylthiophene) is added, and 70 c.c. strong sulphuric acid poured in, the whole being well cooled. The product is allowed to stand some time and then poured into cold water, when an indigo-blue flocculent precipitate is formed; this dissolves in ether without leaving a residue, and may be purified by solution in ether and reprecipitation by light petroleum. The author believes its formula to be  $\text{C}_{19}\text{H}_{12}\text{OS}$  and the reaction representing its formation:—



Sulphur determinations agree with the above formula, but the carbon has up to the present always come out 1—2 per cent. too low; the substance is extremely difficult to burn completely. The colouring matter is a deep-blue powder, having a coppery lustre when compressed. It is soluble to a violet-blue solution in alcohol, benzene, carbon bisulphide, &c., insoluble in water. It is very indifferent to most reagents. Fuming nitric acid dissolves it, and water gives a flocculent brown precipitate with this solution. When it is mixed with powdered lead chromate and heated gradually in a combustion-tube to a dull red heat, anthraquinone distils over. The methyl-group appears to take part in this reaction, as the green colouring matter obtained by V. Meyer (*Ber.*, 16, 2972) from thiophene and phenanthraquinone yielded no anthraquinone under similar treatment. Both bodies yielded phenanthrene when distilled with zinc-dust.

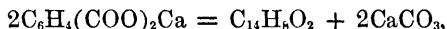
Furfuraldehyde yields similar but less stable compounds with thiophene and methylthiophene; that formed with the latter body is ultramarine-blue in colour.

L. T. T.

**Replacement of Ketonic Chlorine-atoms by Hydrogen.** By B. LACHOWICZ (*Ber.*, 17, 1161—1165).—Dichlorophenanthrone is converted into monochlorophenanthrone by reduction with acetic acid and finely divided iron at 100°. At a temperature of 110°, the product of the reaction is phenanthrone. Under similar treatment, dichlorobenzil yields benzoin chloride,  $C_{14}H_{11}OCl$ , and deoxybenzoin. At temperatures above 90°, tolane tetrachloride is reduced by iron powder and acetic acid to a mixture of  $\alpha$  and  $\beta$  tolane dichlorides.

W. C. W.

**A New Synthesis of Anthraquinone.** By W. PANAOTOVITS (*Ber.*, 17, 312—314).—The author has obtained anthraquinone by the dry distillation of calcium phthalate. The action takes place according to the equation—



and lends support to the di-ketone formula for anthraquinone. The author is now endeavouring to obtain quinone by the dry distillation of calcium fumarate.

L. T. T.

**Chlorinated Anthraquinones. Anthracene from Tetrachlorophthalic Acid.** By G. KIRCHER (*Ber.*, 17, 1167—1170).—When tetrachlorobenzobenzoic acid is treated with a mixture of equal parts of strong and fuming sulphuric acid at 100°, tetrachloranthraquinone and the disulphonic acid are formed. The product is exposed to the air in a flat basin to allow it to attract moisture, and the disulphonic acid is afterwards removed by washing with water. The residual tetrachloranthraquinone,  $C_6Cl_4 : (CO)_2 : C_6H_4$ , is soluble in chloroform, benzene, and carbon bisulphide. It is precipitated from these solutions by alcohol. It crystallises in yellow-coloured needles, melting at 191°. Fuming nitric acid at 140° converts the chloranthraquinone into a mixture of tetrachlorophthalic acid and a nitro-product crystallising in needles which melt at 230°.

*Tetrachloranthracene* is formed by the action of hydriodic acid and

amorphous phosphorus on tetrachlorobenzobenzoic acid at 200°. It is deposited in white needles melting at 148°, when alcohol is added to the solution in chloroform or benzene. On oxidation with chromic acid, tetrachloranthracene yields a tetrachloranthraquinone which melts at 191°. Tetrachloranthracene is converted into dichloranthracene by the action of zinc-dust and ammonia. The dichloro-compound, melting at 255°, by oxidation yields dichloranthraquinone, melting at 261°.

Octochloranthraquinone, described by Panaotovits (this vol., p. 1039) is formed in small quantity in the dry distillation of calcium tetrachlorophthalate.

W. C. W.

**Oxidation of Purpurin.** By C. DRALLE (*Ber.*, 17, 376).—Schunck and Roemer (*Ber.*, 10, 175) pointed out that an alkaline solution of purpurin is bleached by exposure to light. By extracting the colourless solution with ether, the author has detected the presence of phthalic acid. This acid is also formed when an alkaline solution of purpurin or quinazarin is oxidised by potassium ferricyanide. Alizarin, on oxidation, does not yield any crystalline compound soluble in ether.

W. C. W.

#### **$\alpha$ -Nitroanthraquinonesulphonic Acid and its Derivatives.**

By A. CLAUS (*Ber.*, 17, 1276—1279).—In reply to Lifschütz (*Ber.*, 17, 899) the author maintains the correctness of his previous results, and accuses Lifschütz of piracy.

Strumper has now prepared the hydroxy-acid of  $\alpha$ -amidoanthraquinonesulphonic acid, and is investigating its derivatives. On fusing it with potash, it yields alizarin just as the nitro-derivative does.

L. T. T.

**Reply.** By C. LIEBERMANN (*Ber.*, 17, 1279—1280).—The author justifies his having set his students to work on this subject on the ground—1, of having worked on it previous to Claus' reservation, and, 2, that several of the results obtained by Claus and his students are incorrect. He still doubts the existence of Claus' etheric sulphoacids, and the formation of alizarin by the fusion of the nitro-acid with potash.

L. T. T.

**Retene.** By E. BAMBERGER (*Ber.*, 17, 453—456).—After referring to the researches of Wahlforss (*Zeitsch. f. Chem.*, 1869, 74) and Ekstrand (*Annalen*, 185, 75) on retene and dioxyretistene, the author points out that the latter body (which he prefers to call *retistene*—

*quinone*) has the composition  $C_{14}H_{14}$   $\begin{matrix} \diagup CO \\ | \\ \diagdown CO \end{matrix}$ , and forms a series of com-

pounds analogous to those of phenanthraquinone. Retistene-quinone dissolves in hot aqueous solutions of the alkalis, taking up water and yielding a salt of *retistene-glycolic acid*,  $C_{14}H_{14} : C(OH).COOH$ . On oxidation, the acid is converted into *retistene-ketone*,  $C_{14}H_{14} : CO$ , which yields *retistene-fluorene alcohol*,  $C_{14}H_{14} : CH.OH$ , on treatment with zinc and hydrochloric acid.

Retistene-quinone may easily be recognised by the blood-red color-



tion which is produced when a small quantity of alcoholic potash is added to an alcoholic solution of the quinone. The colour disappears if the mixture is shaken with air, but reappears again on warming, in absence of air.

W. C. W.

**Dioxyretistene.** By A. G. EKSTRAND (*Ber.*, **17**, 692—697).—Dioxyretistene has the formula  $C_{32}H_{28}O_4$  or  $C_{32}H_{26}O_4$ , the latter, perhaps, being the more probable. By distillation with 10 times its weight of dry barium hydroxide, dioxyretistene yields a mixture of oil and crystals. The crystalline substance,  $C_{30}H_{26}O_2$ , after purification, is obtained in broad yellow needles, melts at  $90-91^\circ$ , is readily soluble in ether, alcohol, glacial acetic acid, benzene, and light petroleum, yields about half its weight of retene when distilled with zinc-dust, does not unite with hydrogen sodium sulphite, and does not appear to be attacked by boiling alcoholic potash. On oxidation with chromic acid in glacial acetic acid solution, it yields a substance of the formula  $C_{30}H_{22}O_4$ , crystallising in long yellow needles, melting at  $151-152^\circ$ , and insoluble in alkalis. Heated with zinc, this product gives a substance crystallising in small white plates, and melting at  $65-66^\circ$ , but the quantity was too small for further investigation.

By the action of sodium amalgam on an alcoholic solution of the substance  $C_{30}H_{26}O_2$ , a substance of the formula  $C_{30}H_{32}O_2$  is obtained (yield 95 per cent. of theoretical). This crystallises in interlaced white needles, melts at  $134^\circ$ , and by heating with acetic anhydride, yields an acetyl compound, crystallising in white needles, melting at  $70^\circ$ , and giving numbers on analysis best agreeing with the formula  $C_{30}H_{32}(OAc)_2 \cdot C_{30}H_{28}OAc.OH$ . By oxidation with chromic acid or solution in alcoholic potash, the compound  $C_{30}H_{26}O_2$  is again formed. It yields retene when heated with zinc-dust.

From the oil obtained by distilling dioxyretistene with baryta, there were isolated, retene, the compound  $C_{30}H_{26}O_2$  and a hydrocarbon (or mixture of hydrocarbons)  $C_{27}H_{30}$ , distilling between  $290-310^\circ$  without showing a constant boiling point.

Dioxyretistene, when heated with acetic anhydride in sealed tubes for 24 hours at  $170^\circ$ , is converted into a mixture of two substances: tetracetyldioxyretistene,  $C_{32}H_{22}(OAc)_4$ , crystallising in large, hard, green rhombic needles, and an anhydride of dioxyretistene,  $(C_{32}H_{25}O_3)_2O$ , crystallising in needles having a red metallic lustre. Both compounds are sparingly soluble in glacial acetic acid, benzene, and xylene.

A. J. G.

**Isomeric Chloronitro-camphors.** By P. CAZENEUVE (*Compt. rend.*, **98**, 306—307).—When monochlorocamphor is treated with four times its weight of nitric acid, it yields a chloronitro-camphor,  $C_{10}H_{11}Cl(NO_2)O$ , which after purification by crystallisation from alcohol, melts at  $95^\circ$ , and has a specific rotatory power  $[\alpha]_D = -6.2^\circ$  (Abstr., 1883, 667). If the alcoholic mother-liquors from this are strongly cooled, they become semisolid from the deposition of crystals of an isomeric chloronitro-camphor, which may be purified by repeated crystallisation from alcoholic ammonia. It is indistinctly crystalline, melts at  $83^\circ$ , and has a specific rotatory power  $[\alpha]_D = +17^\circ$ , but otherwise closely resembles its isomeride, except that it is soft and plastic,

and is very soluble in cold alcohol. With reducing agents, it gives nitro-camphor, like its isomeride.  
C. E. G.

**Asarone.** By B. RIZZA and A. BUTLEROW (*Ber.*, **17**, 1159—1160).—Pure *asarone* crystallises in needles or plates soluble in alcohol, ether, carbon tetrachloride, acetic acid, and in hot water. It melts at 59°, and boils at 296°. Its sp. gr. at 18° is 1.165. Asarone unites with 2 atoms of bromine to form the addition-product  $C_{12}H_{16}Br_2O_3$ .

The authors state that Gräber's *asarite* does not exist.

W. C. W.

**Daphnetin.** By W. WILL and O. JUNG (*Ber.*, **17**, 1081—1091).—This investigation was undertaken for the purpose of determining the constitutional formula of daphnetin. Stünkel (*Ber.*, **12**, 109) has already shown that it is probably a dihydroxycoumarin, and with a view to prove this and show it to be isomeric with aesculetin, the authors prepared its ethyl-derivatives and the products resulting from them on oxidation. By these means, they show that daphnetin stands in the same relation to pyrogallol as coumarin does to phenol, and as umbelliferone to resorcinol, and that aesculetin may possibly stand in a similar relation to phloroglucol. The results have been confirmed by v. Pechmann (*Ber.*, **17**, 929) by his synthetical formation of daphnetin by the action of malic acid on pyrogallol.

*Ethyl-derivatives of Daphnetin.*—These are formed by boiling an alcoholic solution of daphnetin with ethyl iodide and caustic potash. On evaporating the liquid with water, an oil separates out, which can be extracted with ether. *Monethyldaphnetin*,  $C_9H_5O_3.OEt$ , is found in the aqueous solution, and when crystallised from dilute alcohol, forms colourless plates, melting at 155°, and soluble in alcohol, benzene, and ether. *Diethyldaphnetin*,  $C_6H_4O_2(OEt)_2$ , is obtained from the ethereal extract. It crystallises from alcohol in needles melting at 72°, is soluble in alcohol, ether, and benzene, but insoluble in water. Dilute aqueous soda solution dissolves it only when heated, and from this solution acids reprecipitate it—a property in which it resembles coumarin. *Monobromodiethyldaphnetin*,  $C_{13}H_{13}O_4Br$ , is obtained from diethyldaphnetin by the action of bromine in bisulphide of carbon solution, and forms colourless crystals melting at 115°, and soluble in hot alcohol, in ether, and in benzene. It is insoluble in cold dilute soda solution, but on boiling it with alcoholic potash, hydrobromic acid is eliminated, and, on acidifying the solution, a new acid, diethyldaphnetilic acid, crystallises out. *Diethyldaphnetilic acid*,  $C_{13}H_{14}O_5$ , forms fine asbestos-like crystals melting at 154°. Like coumarilic acid and the analogous compound of umbelliferone and aesculetin, when treated with sodium amalgam, it takes up two atoms of hydrogen and forms a hydrodaphnetilic acid.

By evaporating a solution of diethyldaphnetin in caustic soda to dryness, a yellow crystalline mass is obtained, which is probably the sodium salt of diethyloxycoumaric acid. On heating this salt with ethyl iodide and alcohol in a sealed tube, a neutral oil was extracted from the aqueous solution, which was found to consist of a mixture of unaltered diethyldaphnetin and ethylic triethyldaphnetate. As it was found difficult to obtain the ether pure, it was converted into the

potassium salt, and from the latter the free acid was obtained, and purified from diethylclaphnetin by crystallisation from alcohol. *Triethylclaphnetic acid*,  $C_{15}H_{20}O_5$ , is a white crystalline substance, melting at  $193^\circ$ , and soluble in hot alcohol, ether, and benzene, but insoluble in water and carbon bisulphide. It is formed in the same way as is triethylaesculetic acid, and, like the latter on treatment with sodium amalgam, readily takes up two atoms of hydrogen to form *hydrotriethylclaphnetic acid* or triethyloxyphenylpropionic acid (m. p.  $85^\circ$ ).

On oxidising triethylclaphnetic acid with potassium permanganate, the authors obtained a substance melting at  $70^\circ$ , and giving the reactions of an aldehyde (triethoxybenzaldehyde), and also by further oxidation triethoxybenzoic acid,  $C_{13}H_{18}O_5$ . This acid is insoluble in water, soluble in alcohol, ether, and benzene, and melts at  $100.5^\circ$ . On heating the silver salt in a current of carbonic acid, a distillate was obtained, which quickly solidified, and on purification was found to be a white crystalline compound body, melting at  $39^\circ$ , and by analysis and properties identical with triethylpyrogallol,  $C_{12}H_{18}O_3$ .

A. B.

**Hæmatoxylin and Brazilin.** By C. DRALLE (*Ber.*, 17, 372—378).—*Hæmatoxylin*.—No definite products could be obtained by the action of hydrochloric, hydrobromic, or hydriodic acids, or of chlorine, methyl iodide, or nitrous acid on hæmatoxylin. Dibromhæmatoxylin,  $C_{16}H_{12}Br_2O_6$ , is formed by the action of bromine on a solution of hæmatoxylin in hot acetic acid. It is a crystalline substance, soluble in water and in dilute alkalis, without decomposition. It is decomposed at  $120^\circ$ . The acetic derivative of hæmatoxylin is also attacked by bromine, yielding a crystalline compound of the composition



Brazilin appears to yield a methyl-derivative, which has not yet been isolated. Negative results only were obtained by acting on brazilin with chlorine, bromine, hydrochloric, hydrobromic, and sulphuric acids.

W. C. W.

**Hæmatoxylin and Brazilin.** By K. BUCHKA (*Ber.*, 17, 683—685).—Dralle has recently prepared dibromhæmatoxylin and tetrabromopentacetylhæmatoxylin, but states that he could not obtain crystalline compounds by the action of bromine on brazilin or acetyl-brazilin (preceding Abstract).

*Monobromacetylhæmatoxylin*,  $C_{16}H_8BrO_6\overline{Ac}_3$ , prepared by adding bromine dissolved in glacial acetic acid, drop by drop, to a cold solution of acetylhæmatoxylin in glacial acetic acid, allowing to stand for some hours, precipitating with aqueous sulphurous acid, and crystallising from alcohol, forms slender colourless needles; it melts at  $210^\circ$ , and is soluble in chloroform, glacial acetic acid, and benzene. By heating with alkalis, it is converted into bromhæmatoxylin. By the action of bromine on a boiling solution of hæmatoxylin in glacial acetic acid, a dark red crystalline substance is obtained; it is now under investigation.

*Monobromacetylbrazilin*,  $C_{16}H_9BrO_5\overline{Ac}_4$ , prepared in a manner similar

to that above described for the corresponding hæmatoxylin compound, crystallises in slender silky needles; it melts at 203—204°, is converted into bromobrazilin by aqueous potash, and on treatment with bromine at 100° is converted into a red crystalline substance, which will be further examined.

A. J. G.

**Action of Acetic Anhydride and Benzoic Anhydride on Pyrroline.** By G. L. CIAMICIAN and M. DENNSTEDT (*Ber.*, 17, 432—433).—In a previous communication, the authors pointed out that two isomeric compounds are formed by the action of acetic anhydride on pyrroline. Pseudacetopyrroline contains one atom of hydrogen replaceable by silver. By boiling a methyl alcohol solution of pseudacetopyrroline with hydroxylamine hydrochloride and sodium carbonate, a substance is obtained which melts at 145°, and has the constitution  $\text{HON} : \text{CMe} \cdot \text{C}_4\text{H}_3 : \text{NH}$ . This shows that the formula for pseudacetopyrroline is  $\text{CH}_3\text{CO} \cdot \text{C}_4\text{H}_3 : \text{NH}$ . Acetic anhydride at 250° converts pseudacetopyrroline into a compound,  $\text{C}_4\text{H}_2\text{Ac}_2\text{NH}$ , which contains one atom of hydrogen replaceable by silver. This body melts at 161°.

Benzoic anhydride resembles acetic anhydride in its action on pyrroline. It yields two compounds, one liquid, the other crystalline, melting at 75°. The latter forms a silver compound. The constitution of the solid isomeric is represented by the formula

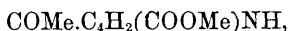


W. C. W.

**$\alpha$ -Carbopyrrolic Acid.** By G. L. CIAMICIAN and P. SILBER (*Ber.*, 17, 1150—1158).— $\alpha$ -Carbopyrrolic acid can be prepared by heating pyrroline with water and ammonium carbonate in sealed tubes at 140°. The product is gently evaporated to expel ammonium carbonate and pyrroline, and when cold is acidified with dilute sulphuric acid and extracted with ether. The acid is purified by recrystallisation from alcohol. If the temperature rises above 140° in the preparation of the acid, a small quantity of a second acid, probably  $\beta$ -carbopyrrolic acid, is also formed. The *calcium* salt of the  $\alpha$ -acid,  $\text{Ca}(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_4)_2$ , forms white scales. The *silver* salt is sparingly soluble. The *methyl* salt,  $\text{C}_5\text{H}_4\text{MeNO}_2$ , crystallises in needles or prisms, melting at 73°, and soluble in ether and alcohol. The *ethyl* salt melts at 39°, and boils at 231°. It dissolves freely in alcohol, ether, and benzene. Methyl tribromocarbopyrrolate is formed when bromine vapour is passed into a hot aqueous solution of methyl  $\alpha$ -carbopyrrolate. It forms crystalline needles, melting at 210°, and soluble in ether and hot alcohol. On saponification, it yields tribrom- $\alpha$ -carbopyrrolic acid; this is deposited from a hot aqueous solution in needles which are freely soluble in ether, alcohol, and acetone. The acid begins to decompose at 140°.

A crystalline compound, probably  $\text{NH} : \text{C}_4\text{H}_3\text{COO} \cdot \text{COMe}$ , is obtained by the action of acetic chloride on silver carbopyrrolate suspended in light petroleum. It is decomposed by water into acetic and carbopyrrolic acids. It melts at 75°, and at a higher temperature splits up into acetic acid and pyrocoll.

The *methyl salt of pseudacetyl- $\alpha$ -carbopyrrolic acid*,



is formed when methyl carbopyrrolate is heated in sealed tubes at  $250^\circ$ , with acetic anhydride. It is deposited from a hot aqueous solution in glistening needles, melting at  $113^\circ$ , soluble in alcohol and ether. It contains one atom of hydrogen replaceable by silver. The free acid forms vitreous plates, melting at  $186^\circ$ ; it dissolves in water, ether, alcohol, and acetone. The silver salt is sparingly soluble. The calcium salt,  $\text{Ca}(\text{C}_7\text{H}_5\text{NO}_3)_2 + 7\text{H}_2\text{O}$ , forms triclinic crystals.

W. C. W.

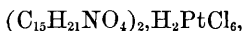
**Pyrroline Dyestuffs.** By V. MEYER and O. STADLER (*Ber.*, **17**, 1034—1036).—The blue dyestuff obtained by the action of pyrroline on isatin (this vol., 587) has been purified as much as possible and analysed. The results of analysis agree with those of Ciamician and Silber (this vol., 740) as far as concerns the carbon and hydrogen. The quantity of nitrogen, however, found is smaller by 1.9 per cent. than that required by Ciamician and Silber's formula ( $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_3$ ). These authors have given no results of the nitrogen determinations. It is therefore doubtful whether the reaction is as simple as that expressed by their equation.

The authors also find that reactions with formation of dyestuffs take place between phenanthraquinone and pyrroline, and between benzoquinone and pyrroline.

A. B.

**Decomposition-products of the Pyrroline Series.** PART I. By A. HANTZSCH (*Ber.*, **17**, 1019—1032).—It has been shown by Hofmann that the ammonium-compounds of bases are often found to be capable of being split up into less complicated substances, whilst the bases themselves are not. Conine and piperidine are examples of this. The decomposition of pyridine ammonium-compounds by potash is, however, more complicated, and the compounds obtained are very unstable. In the hope of obtaining more stable decomposition-products, the author has been led to study the decomposition of the ammonium-derivatives of ethylic collidinedicarboxylate by potash and in other ways, this member of the pyridine series being chosen on account of the ease with which it can be synthetically prepared (*Abstr.*, 1883, 83).

*Methiodide of ethylic collidinedicarboxylate*,  $\text{C}_5\text{Me}_3(\text{COOEt})_2\text{N.MeI}$ , is obtained by heating the ether with methyl iodide for several hours in a sealed tube, dissolving the resulting ammonium-compound in alcohol, and precipitating with ether. It is readily soluble in water and alcohol, is not hygroscopic, melts at  $140^\circ$ , and decomposes at  $160^\circ$ . Silver chloride converts it into the corresponding chloride, and with platinic chloride it gives a platinochloride,



as an oil, which may be obtained in a crystalline form, but only with difficulty. The salts of this ammonium base have an acid reaction, are not decomposed by ammonia, as are the salts of the non-methylated

base, but the salt is precipitated unchanged by potassium carbonate. The hydroxide,  $C_5Me_3(COOEt)_2N, MeOH$ , is obtained by treating the chloride or iodide with silver oxide. It is an alkaline liquid, which rapidly decomposes, becoming black, and forming along with by-products a crystalline substance, which, however, can be more readily obtained without the formation of by-products, by decomposing a salt of the base with potash.

*Decomposition of the Methyl Ammonium Salt by Potash.*—When the ammonium salt of ethyl collidinedicarboxylate is heated with concentrated potash solution, a yellow oil is precipitated, which rapidly solidifies, and may be purified by crystallisation from water or ether. This substance is soluble in alcohol, ether, chloroform, and benzene, and in hot water, and melts at  $81.5^\circ$ . It has no odour, distils above  $360^\circ$  without decomposition, and is remarkable for its chemical indifference. Its aqueous solution is precipitated by alkalis, but it is unchanged by boiling with potash. It has a neutral reaction, and does not form salts with acids or bases. It is also unattacked by concentrated hydrochloric acid, or by acetic anhydride. Analysis leads to the formula  $C_{11}H_{13}O_4N$ . Owing to the indifference of this substance, a proof of the constitutional formula is difficult, but the ether seems to be saponified, and also to lose a molecule of water, and the author calls it *methyl dicarbocollidylum dihydride*.

*Action of Acids on Methyl dicarbocollidylum Dihydride.*—On passing dry hydrochloric acid over this dihydride, a molecule of  $HCl$  is taken up, which, however, is removed by treatment with water. On heating this hydrochloride in a current of dry hydrochloric acid gas, it distils in part, and the distillate, on being treated with water and evaporated to dryness, yields on further treatment with potassium carbonate and extraction with ether, a new crystalline compound,  $C_{10}H_{13}O_2N$ , soluble in the ordinary solvents, melting at  $102-103^\circ$ , and distilling at about  $340^\circ$ . It may be considered as methyl monocarbocollidylum dihydride. Like the dicarbo-compound, it is neutral and indifferent, and resists the action of alkalis and other reagents.

On acting on these carbo-compounds with concentrated sulphuric acid at  $160-180^\circ$ , acetic acid is given off, and a new substance is obtained, according to the equations  $C_{10}H_{13}O_2N + H_2O = CH_3.COOH + C_8H_{11}ON$  and  $C_{11}H_{13}O_4N + H_2O = CH_3.COOH + CO_2 + C_8H_{11}ON$ . These reactions are quantitative, and the author names this compound in accordance with Baeyer's nomenclature of the isatin-compounds

“*methyl pseudolutidostyryl*,”  $MeC \begin{smallmatrix} CH.CMe \\ -CH.CO- \end{smallmatrix} NMe$ .

*Methyl pseudolutidostyryl* crystallises in six-sided plates, is very soluble in water, soluble in alcohol and benzene, but very sparingly in ether. It melts at about  $70^\circ$ , and distils without decomposition at  $292^\circ$ . The distillate solidifies to a white spermaceti-like mass, which is very hygroscopic. It has neither taste nor smell, and is not volatile in steam. Concentrated potash solution precipitates it from its aqueous solution, but does not attack it even on heating; on prolonged boiling, however, it is decomposed by potash, with formation of methylamine and other decomposition-products. As a tertiary base it is soluble in acetic anhydride, without evolution of heat, but is unchanged, and it forms

no nitroso-compound. Although neutral, it forms salts with mineral acids; these have the formula  $(C_8H_{11}ON)HX'$ , and are readily converted into basic salts,  $(C_8H_{11}ON)_2HX'$ , in presence of ammonia: in this it resembles some derivatives of cotarnine (Abstr., 82, 315). The hydrochloride of methylpseudolutidostyryl crystallises from water in long needles, of the formula  $C_8H_{11}ON.HCl + \frac{1}{2}H_2O$ . With fuming hydriodic acid, it forms a normal hydriodide, but on adding water a precipitate of fine yellow needles of the basic salt  $(C_8H_{11}ON)_2HI$  is formed. The platinochlorides are characteristic. On treating an alcoholic solution of the base with alcoholic platinic chloride, a crystalline precipitate of slender yellow needles is obtained, consisting of a neutral platinochloride with two molecules of alcohol of crystallisation,  $(C_8H_{11}ON)_2.H_2PtCl_6 + 2C_2H_5O$ . From an aqueous solution of the base, platinic chloride precipitates the same platinochloride, with 2 mols.  $H_2O$ , along with some basic salt. Chromic acid completely decomposes the base. With bromine, it forms a dibromo-compound,  $C_8H_9Br_2ON$ , melting at  $173^\circ$ , sparingly soluble in water, but soluble in alcohol and ether. Phosphorus pentachloride does not eliminate the oxygen of the base, but yields a chlorine-derivative,  $C_8H_9ClON$ , melting at  $187^\circ$ ; this may also be obtained by the direct action of chlorine. With methyl iodide at  $120^\circ$ , a reaction takes place, but the ammonium-compound seems to be very unstable, readily decomposing into the original pseudostyryl, and in this it differs from the corresponding derivative of tropine (Abstr., 1882, 217). It is not reduced by tin and hydrochloric acid, nor by sodium amalgam and acetic acid. Cold fuming nitric acid does not attack it, but at  $45^\circ$  a violent reaction takes place, and the pseudostyryl is partly decomposed, with formation of oxalic acid, and partly converted into a nitro-derivative, which is more easily formed by boiling it with dilute nitric acid.

The action of hydrochloric acid and of potassium permanganate on methylpseudolutidostyryl will form the subject of a future paper.

A. B.

**Synthesis of Pyridic Hydrides.** By O. DE CONINCK (*Compt. rend.*, 98, 1438—1440).—When  $\beta$ -lutidine and  $\beta$ -collidine are heated in sealed tubes with an excess of concentrated hydriodic acid at  $220^\circ$  for several hours, they yield polyiodides which are very viscous brown liquids and boil at a high temperature with partial decomposition. They are either triiodides or hydriodides of di-iodides.

$\beta$ -Collidine heated in sealed tubes at  $130$ — $140^\circ$  with amorphous phosphorus and concentrated hydriodic acid, yields a small quantity of dihydrocollidine. This base yields a platinochloride which forms pale orange-yellow plates, readily altered by boiling water.

When treated with sodium and alcohol under certain conditions,  $\beta$ -lutidine yields a small quantity of a hexhydride,  $C_7H_{15}N$ , which boils at about  $155$ — $160^\circ$ , is very hygroscopic, and can only be separated from the original lutidine with considerable difficulty. It is a colourless mobile refractive liquid, which resembles the other pyridines in appearance, and has a peculiar penetrating odour recalling that of piperidine. It combines with methyl iodide to form a crystalline compound which yields a small quantity of a cicutine,  $C_8H_{17}N$ , when distilled with a slight excess of potash. This cicutine probably has

the constitution  $C_5H_9EtNMe$ , and is isomeric with ordinary cicutine or orthopropylpyridine hexhydride.

Under similar conditions,  $\beta$ -collidine yields a hexhydride,  $C_8H_{17}N$ , boiling about  $175-180^\circ$ . This hydride is difficult to separate from the collidine, and is very hygroscopic. The behaviour of  $\beta$ -collidine on oxidation shows that it is methyl-ethyl pyridine, and the new hydride has the constitution  $C_5H_5MeEtNH$ , and is therefore another isomeride of cicutine.

C. H. B.

**Isopropylpyridines.** By A. LADENBURG and L. SCHRADER (*Ber.*, **17**, 1121—1123).— $\gamma$ -Isopropylpyridine boils at  $158^\circ$ , and has the sp. gr. 0.9408 at  $0^\circ$ . It is slightly soluble in water. The hydrochloride is hygroscopic, the platinochloride has not yet been obtained in crystals. The aurochloride is deposited from hot water in orange needles which melt at  $79^\circ$ . The base unites with methyl iodide to form a crystalline hygroscopic compound. The aurochloride of the methyl base forms pale-yellow plates which melt at  $128^\circ$ .  $\gamma$ -Isopropylpyridine, when oxidised with potassium permanganate, yields  $\gamma$ -pyridine-carboxylic acid melting at  $303^\circ$ .

The isomeric isopropylpyridine (probably  $\alpha$ ) boils at about  $167^\circ$ . The platinochloride forms four-sided plates melting at  $206^\circ$ , which are less soluble than the corresponding  $\gamma$ -salt. The base appears to be identical with Hofmann's conyryne from conine (*Ber.*, **17**, 825). On reduction with sodium and alcohol, it yields a base resembling conine, hence the authors consider it probable that conine is  $\alpha$ -isopropylpiperidine.

W. C. W.

**Notes.** By E. NÖLTING and A. COLLIN (*Ber.*, **17**, 258—259).—I. *Pyridinedicarboxylic acid*, obtained by the oxidation of quinoline by potassium permanganate, has the two carboxyl-groups in the *ortho*-position, and may therefore be regarded as phthalic acid in which one CH-group has been replaced by N. Like phthalic acid, it combines with phenols. When heated at  $120^\circ$  with phenol and sulphuric acid, it forms a condensation-product which dissolves in alkalis to a red solution. By the action of resorcinol at  $200^\circ$ , it yields a body similar in character to fluorescein, and this on bromination gives a red colouring matter resembling eosin.

II. *Blue Colouring Matters from Rosaniline*.—It is well known that a blue colouring matter is obtained when aniline, or *ortho*- or *para*-toluidine is heated with rosaniline and benzoic acid. Metatoluidine yields a similar crystalline blue dye soluble in alcohol, insoluble in water, and giving a sulphonic acid.  $\beta$ -Naphthylamine, under similar conditions, also yields a blue, already described by Meldola (*Abstr.*, 1883, 807). The authors have attempted to find some cheaper substitute for the excess of aniline at present used in preparing these colouring matters on a commercial scale. Naphthalene may be used to replace aniline, but this change has not proved commercially useful.

L. T. T.

**Derivatives of Quinoline and Pyridine.** By O. FISHER and E. RENOUF (*Ber.*, **17**, 755—764).—A continuation of the authors' researches on this subject (*Abstr.*, 1883, 923—1146).



*Oxidation of Orthoquinolinesulphonic Acid.*—By the oxidation of 40 grams of this substance with potassium permanganate in aqueous solution 23 grams of quinolic acid were obtained. Orthhydroxyquinoline (40 grams) also yields quinolic acid (20 grams) on oxidation with aqueous potassium permanganate.

*Orthhydroxyhydroethylquinoline.*—The preparation of this substance has been already described; it crystallises in colourless monoclinic prisms showing the combinations  $\infty P\infty$ ,  $\infty P\infty$ ,  $-P$ ,  $\infty P$  and  $P\infty$ . Axial ratios  $a : b : c = 0.9711 : 1 : 1.3549$ .  $\beta = 72^\circ 54'$ . It melts at  $76^\circ$ , can be distilled unchanged in small quantity; the vapour has a penetrating odour somewhat recalling that of ethylamine. It is rapidly oxidised when its alkaline solution is exposed to air, humus-like substances being formed. Its alcoholic solution gives a dark-brown coloration with ferric chloride, and a dark greenish-black flocculent precipitate with ferrous sulphate. An acid solution gives a voluminous precipitate with potassium ferrocyanide, a pale-yellow precipitate with phosphotungstic acid, whilst with sodium nitrite an intense yellow colouring matter is formed. Its hydrochloride, "kairin," forms colourless rhombic prisms of the rhombic system,  $a : b : c = 0.5945 : 1 : 0.9566$ , and shows the combination  $\infty P$ ,  $\infty P\infty$ ,  $\infty P2$ ,  $P12$ ,  $\frac{3}{2}P\infty$ . With potassium dichromate, a neutral aqueous solution of kairin gives first a dark coloration, and after a few seconds a dark-violet precipitate soluble in alcohol with a mauve-like colour; with potassium ferricyanide, a dark yellowish-green coloration is produced.

*Ethoxyquinoline* has been already in part described (*loc. cit.*). It distils in a current of steam with difficulty, and is obtained from the distillate in long colourless needles. The sulphate, oxalate, and hydrochloride are readily soluble in water and alcohol. The picrate crystallises in sulphur-yellow needles, melts at  $180-181^\circ$ , and is sparingly soluble in water and alcohol.

*Ethoxyhydroquinoline.*—The nitroso-derivative crystallises in short prisms and melts at  $113^\circ$ . The hydrochloride crystallises in colourless prisms; the oxalate forms colourless cubes; the sulphate crystallises in long needles, readily soluble in water; the picrate forms orange-yellow prisms sparingly soluble in water, soluble in alcohol.

*Acetylethoxyhydroquinoline*,  $C_{11}H_{14}NOAc$ , prepared by the action of acetic anhydride on ethoxyhydroquinoline, forms a clear yellow oil boiling at  $307^\circ$ . It has a neutral reaction. On boiling it with concentrated mineral acids, the acetyl-group is eliminated.

*Ethoxyhydroethylquinoline*,  $C_{13}H_{19}NO$ , is prepared by heating ethyl bromide and ethoxyhydroquinoline for some hours under pressure at  $120-130^\circ$ . It crystallises in colourless silky plates, melts at  $33^\circ$ , boils at  $266-268^\circ$  under 716 mm. pressure, and is readily soluble in the ordinary solvents with the exception of water. The hydrochloride and hydrobromide form colourless plates, the sulphate crystallises in needles; all three are readily soluble. The picrate forms orange-yellow prisms sparingly soluble in alcohol and water.

*Bromethoxyhydroquinoline*,  $C_{11}H_{14}NOBr$ , is prepared by adding the calculated quantity of bromine dissolved in chloroform to a well-cooled solution of ethoxyhydroquinoline in chloroform. It forms lustrous crystals of the triclinic system  $a : b : c = ? : 1 : 0.8101$   $\alpha = 107^\circ 48'$ .

$\beta = 110^\circ 58'$ ;  $\gamma = 85^\circ 0'$ . Some of the best formed crystals showed the combination  $\infty P\infty$ ,  $\infty \bar{P}\infty$ ,  $0P$ ,  $\bar{P}\infty$ . It melts at  $44.5^\circ$ , and at  $150^\circ$  decomposes with almost explosive violence, has basic properties, and forms crystalline salts. The hydrochloride and hydrobromide crystallise in needles, the sulphate in plates: the oxalate in prisms. The picrate forms sulphur-yellow needles, melts at  $107$ – $108^\circ$ , and is sparingly soluble in water and alcohol. The nitrosamine crystallises in lustrous yellow plates and melts at  $86^\circ$ .

*Bromethoxyhydroethylquinoline*,  $C_{13}H_{18}NOBr$ , crystallises in prisms of the monoclinic system  $a : b : c = 0.7902 : 1 : 0.5828$ ,  $\beta = 69^\circ 55'$ , and shows the combination  $\infty P$ ,  $\infty P\infty$ ,  $P\infty$ ,  $\frac{2}{3}P\infty$ . The hydrochloride and hydrobromide crystallise in needles; the picrate in yellow needles melting at  $174^\circ$ . Towards nitrous acid, the bromo-derivative acts as a tertiary base, giving an intensely yellow solution from which sodium carbonate throws down a brownish-yellow substance melting at  $85$ – $86^\circ$ .

$\beta$ -*Hydroxypyridine*,  $C_5H_5NO$ , is prepared from pyridinesulphonic acid by carefully mixing it with twice its weight of caustic potash and fusing in a silver crucible. It crystallises in very pale-yellow needles, melts at  $123.5^\circ$ , sublimes unchanged, and is readily soluble in water and alcohol. Its salts are very soluble. In aqueous solution, it gives a red coloration with ferric chloride; if boiled with excess of the reagent, yellowish-brown crystals separate. Sodium amalgam reduces it to piperidine, and it yields pyridine when distilled with zinc. The foregoing reactions show that it is not identical with the hydroxypyridine of Lieben and Haitinger (Abstr., 1883, 870) and Ost, or with the  $\alpha$ -hydroxypyridine of Konigs and Geigy (Ber., 17, 589).

By treatment with bromine in aqueous solution, it yields a bromo-derivative crystallising in nodules of fine colourless needles; these melt at  $58^\circ$ , and yield a violet coloration with ferric chloride.

A. J. G.

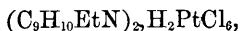
**Method for the Synthesis of Quinoline-derivatives.** By L. RUGHEIMFR (Ber., 17, 736–739).—Malonanilidic acid (1 part) is suspended in 10 parts of anhydrous benzene and 4 parts of phosphorous pentachloride slowly added with constant agitation; the mixture, after remaining some time in the cold, is heated on the water-bath in a vessel provided with a reflux condenser until the evolution of hydrochloric acid ceases. The benzene is first distilled off, and the residue is treated with water and sodium carbonate when trichloroquinoline distils over. *Trichloroquinoline*,  $C_9H_4NCl_3$ , crystallises in long colourless needles, melts at  $107.5^\circ$  (uncorr.), is readily soluble in benzene, light petroleum, and hot alcohol, less soluble in cold alcohol. When gently heated, it smells distinctly like quinoline. It is converted into quinoline by heating it for six hours at  $240^\circ$  with glacial acetic acid saturated with hydriodic acid.

A. J. G.

**Bases formed by the Addition of Haloïd Ethereal Salts to Quinoline.** By A. CLAUS and P. STEGELITZ (Ber., 17, 1328–1333).—It has been previously shown (Abstr., 1883, 1008) that the haloïd salts of the substituted quinolines are identical with the compound formed by the addition of the corresponding haloïd ethereal salts to

quinoline. With the view of throwing light on the constitution of these bodies the authors have investigated their behaviour towards nascent hydrogen.

Quinoline ethobromide was subjected to the action of sodium amalgam, and also to that of tin and hydrochloric acid. The reaction was the same in both cases, but better results were obtained with the acid than with the alkaline solution. Two bases were formed, the one volatile with steam, the other not. The volatile base is a colourless oil, boils at 254—258° with partial decomposition, and is identical with Wischnegradsky's ethyltetrahydroquinoline (*Ber.*, 13, 2400). It is easily soluble in alcohol and ether, almost insoluble in water. It dissolves in mineral acids, but the salts are exceedingly hygroscopic and could not be obtained in a crystalline form. The hydrochloride is dissociated even on evaporation in a desiccator over lime, and is only stable in presence of excess of hydrochloric acid. The platinochloride crystallises in golden-yellow needles having the formula



and melts with decomposition at 160°. A cadmium double salt,  $(C_9H_{10}EtN)_2, H_2CdCl_4$ , melting at 105°, and an analogous salt with mercuric chloride which melts at 65°, were also obtained. The base combines readily with methyl iodide to form a quaternary iodide of the formula  $C_9H_{10}EtN, MeI$ . This forms colourless crystals melting at 179° (uncorr.), and is not acted on by alcoholic potash. Treated with silver oxide, it yields an easily soluble crystalline hydroxide. A platinochloride of the last-named base was obtained which crystallises in small yellow needles, melts at 215°, and has the formula

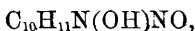


The non-volatile base was obtained as a thick and almost colourless oil. It dissolves readily in dilute acids, and the solutions rapidly change to red or blue, but no crystalline salts could be obtained. Dry hydrochloric acid gas passed into an ethereal solution of the base, gives a white flocculent precipitate, which was obtained as an amorphous powder melting at 140°. It was, however, so hygroscopic that it could not be analysed. The platinochloride, which forms a bright-red powder, was the only product obtained suitable for analysis. The analytical results led to the unexpected formula  $(C_9H_8EtN)_3, H_2PtCl_6$ . The authors therefore consider this base to be a condensation-product from 3 mols. of ethylquinoline, with the addition of 6 atoms of H, but which is only a divalent base. The substance known as hydrodiquinoline is probably also a dibasic hydrotriquinoline. Attempts to obtain oxidation-products from the non-volatile base have, up to the present, proved fruitless, oxalic acid alone having been isolated. L. T. T.

**Paraquinolinesulphonic Acid and its Homologues.** By O. FISCHER and C. A. WILLMACK (*Ber.*, 17, 440—442).—*Paracyanoquinoline*, prepared by the action of potassium cyanide on potassium paraquinolinesulphonate, is a crystalline body which melts at 131°, and sublimes without decomposition. It dissolves in hydrochloric acid, forming a red solution. By the action of strong hydrochloric

acid at  $140^{\circ}$  it is converted into *paraquinolinecarboxylic acid*; this is identical with Schlosser and Skraup's paraquinolinebenzocarboxylic acid (*Monatsh.*, **2**, 526).  $\gamma$ -Methyl- $\alpha$ -quinolinesulphonic acid is obtained by boiling a mixture of paramido-meta-sulphotoluic acid, glycerol, sulphuric acid, and nitrobenzene. The crystalline mass deposited on cooling is washed with water and recrystallised from hot water. It crystallises in colourless plates sparingly soluble in water. If fused with sodium hydroxide, it yields  $\alpha$ -hydroxy- $\gamma$ -methylquinoline. This compound forms colourless plates, soluble in alcohol and in ether. It melts at  $95^{\circ}$  and sublimes without decomposition; it is also volatile in a current of steam. The hydrochloride is freely, and the platinochloride sparingly soluble in water.

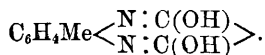
$\alpha$ -Hydroxy- $\gamma$ -methylquinoline tetrahydride crystallises in colourless needles soluble in hot benzene. The nitroso-derivative,



forms small yellow needles.

W. C. W.

**Quinoxalines.** By O. HINSBERG (*Ber.*, **17**, 318—323).—In a former communication (*Abstr.*, 1883, 323) the author described a substance of the formula  $\text{C}_8\text{H}_8\text{N}_2\text{O}_2$ , which he obtained by the condensation of [3 : 4] diamido-toluene and oxalic acid, but was unable to obtain from it a non-oxidised base by reduction. He has now obtained the base of this substance by acting on an aqueous solution of glyoxal with [3 : 4] diamido-toluene. He has also obtained its lower homologue from glyoxal and orthophenylenediamine, and he finds that the reaction is quite general, any ortho-diamine appearing to react with any body containing the di-ketone group  $-\text{CO}\cdot\text{CO}-$  to form derivatives of the simplest base,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{N}:\text{CH} \\ \text{N}:\text{CH} \end{smallmatrix}\rangle$ . He therefore proposes to call this series of compounds *quinoxalines*. The formula of quinoxaline (the lowest homologue) is undoubtedly  $\text{C}_8\text{H}_6\langle\begin{smallmatrix} \text{N}:\text{CH} \\ \text{N}:\text{CH} \end{smallmatrix}\rangle$ , that of the original dihydroxy-derivative,  $\text{C}_8\text{H}_8\text{N}_2\text{O}_2$ , is



*Quinoxaline*,  $\text{C}_8\text{H}_6\text{N}_2$ , is obtained by treating an aqueous solution of glyoxal with orthophenylene diamine, or by adding the crystalline compound of glyoxal and hydrogen sodium sulphite to a solution of the diamine heated to  $50-60^{\circ}$ . The crystals dissolve readily, quinoxaline is formed, and may be separated by adding strong potash. The quinoxaline is dissolved in a little ether, dried over caustic potash, and distilled. It boils at  $220-223^{\circ}$ , and solidifies to a white crystalline mass melting at  $27^{\circ}$ . It is soluble in all proportions in alcohol, ether, benzene, and cold water, but is deposited from its concentrated aqueous solution when heated or on the addition of a caustic alkali. In odour it resembles the piperidine- more than the quinoline-derivatives. Solutions of the free base give white precipitates with silver nitrate and with mercuric chloride. Its salts with mineral acids are easily soluble; the oxalate crystallises in sparingly soluble white

needles, and the platinochloride forms small yellow needles. Nitrous acid is without action, showing that the nitrogen-atoms are in the tertiary state. It is very stable against oxidising agents, but appears to form a nitro-derivative with strong nitric acid. It is easily reduced by tin and zinc.

*Toluoquinoxaline*,  $C_6H_3Me \begin{smallmatrix} N:CH \\ N:CH \end{smallmatrix} > [CH_3 : N : N = 1 : 3 : 4]$ , obtained from [3 : 4] diamidotoluene and glyoxal, is a pale-yellow liquid, which boils at 243—244°, and does not solidify at  $-10^\circ$ . It is heavier than water, and is soluble in all proportions in alcohol, ether, benzene, and cold water. It is precipitated from its aqueous solutions by heat or the addition of a caustic alkali. In its reactions, it resembles quinoxaline, but is less stable towards oxidising agents. Its salts with mineral acids are easily soluble. The oxalate,  $C_{11}H_{10}N_2O_4$ , is sparingly soluble in cold water, and crystallises in needles which melt at 135—136°, but undergo slow decomposition if kept at this temperature.

*Methylhydroxytoluoquinoxaline*,  $C_6H_3Me \begin{smallmatrix} N: CMe- \\ N: C(OH)- \end{smallmatrix} >$ , was obtained from the [3 : 4] diamido-toluene and pyruvic acid. It crystallises from dilute alcohol in small bright yellow needles, but can be obtained colourless by careful sublimation. It melts at about 200° with partial decomposition. It is sparingly soluble in water, more easily so in ether, benzene, and chloroform, very soluble in alcohol. It has both feebly basic and acid properties, dissolving in both mineral acids and in alkalis, and it gives precipitates with ammonia and barium chloride and with ammonia and silver nitrate.

*Diphenyltoluoquinoxaline*,  $C_7H_6 : N_2C_2Ph_2$ , is obtained in the form of brownish silver-like scales when a mixture of [3 : 4] diamidotoluene and benzil is heated for some time on the water-bath and then diluted with water. It distils undecomposed, and melts at 111°, is almost insoluble in water, but dissolves easily in alcohol, ether, chloroform, and benzene. It dissolves in concentrated mineral acids, but the salts so formed are again decomposed on the addition of water.

*Diphenylenetoluoquinoxaline*,  $C_7H_6 \begin{smallmatrix} N: C-C_6H_4 \\ | \quad | \\ N: C-C_6H_4 \end{smallmatrix}$ , is prepared by pouring an alcoholic solution of [3 : 4] diamido-toluene into a warm acetic solution of phenanthraquinone. It forms bright yellow needles, which melt at 212—213°. It is insoluble in water, sparingly soluble in alcohol, easily so in ether, chloroform, and benzene. Concentrated mineral acids yield deep-red salts, which are decomposed by water.

L. T. T.

**Dimethylquinaldine.** By L. BEREND (*Ber.*, 17, 653).—Dimethylquinaldine is obtained by the action of paraldehyde on xylylidine from orthoxylene. It melts at 69—70°, is scarcely soluble in water, readily soluble in ether, alcohol, and benzene.

A. J. G.

**Dimethylquinaldine.** By W. MERZ (*Ber.*, 17, 1158).—A question of priority.

**Aldehyde-collidine Hexahydride.** By E. DÜRKOPF (*Ber.*, **17**, 1131—1132).—Aldehyde-collidine is converted into the hexahydride by the action of sodium in presence of absolute alcohol. The product is distilled, and the hydrochloric acid is added to the distillate in order to separate the hydride from the unaltered collidine. When the hydrochloride is mixed with potash and distilled in a current of steam, the hydride is obtained as an oily liquid boiling at 165°.

W. C. W.

**Cystine.** By J. MAUTHNER (*Ber.*, **17**, 293—295).—By the action of water on cystine in closed tubes at 140—150°, the author has obtained an acid containing sulphur but no nitrogen. Analyses of the silver salt yielded numbers which leave it doubtful whether the acid has the formula  $C_6H_{10}S_2O_4$  or  $C_6H_8S_2O_4$ . Carbonic anhydride, sulphuretted hydrogen, and ammonia were formed in this reaction, and a trace of mercaptan was also detected by its odour. The author will continue his investigations after the publication of Baumann's promised communication on cystine.

L. T. T.

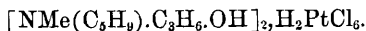
**Synthesis of Piperidine and its Homologues.** By A. LADENBURG (*Ber.*, **17**, 388—391).—*Methylpiperidine*,  $C_5H_9MeNH$ , isomeric with Hofmann's *methylpiperidine*,  $C_5H_{10}NMe$ , is formed by the action of sodium on an alcoholic solution of picoline from bone-oil. After purification by conversion into the nitroso-compound, methylpiperidine is an oily liquid which boils at 121—124°. It is soluble in water, forming a strongly alkaline solution. The aurochloride, platinochloride, and hydrochloride of this base are crystalline salts, freely soluble in water. The hydrochloride does not yield precipitates with mercuric chloride or potassium ferrocyanide. This reaction distinguishes it from its isomeride.

$\gamma$ -Ethylpiperidine, prepared from  $\gamma$ -ethylpyridine, is sparingly soluble in water, less soluble in warm than in cold water. The hydrochloride crystallises in needles, and the platinochloride in orange-coloured plates.

W. C. W.

**Piperpropylalkine.** By W. LAUN (*Ber.*, **17**, 680—683).—In preparing piperpropylalkine, the use of sealed tubes is not necessary, it being sufficient to heat the mixture of propylene chlorhydrin and piperidine for four hours on the water-bath in a vessel provided with a reflux condenser. It boils at 194°, has sp. gr. 0.9456 at 0° and 0.9363 at 10°, vapour-density 4.79.

*Piperpropylalkine methiodide*,  $C_8H_{17}NO, MeI$ , forms a colourless somewhat hygroscopic crystalline mass, and melts at 142°. Treated with silver chloride, it yields the corresponding chloride, from which the platinochloride and aurochloride can be prepared. With moist silver oxide, the ammonium base,  $NH(C_3H_7)(C_3H_6.OH)Me.OH$ , is formed; this on distillation loses the elements of water, and is converted into the corresponding methylated piperpropylalkine, whose platinochloride gave numbers agreeing with the formula



The methylated base could not be isolated, as by the action of potash it is resolved into methylpiperidine and propylene glycol?

*Benzoylpiperpropylalkaline*,  $N(C_5H_{10})C_3H_6.OBz$ , is obtained as hydrochloride by the action of benzoic chloride on piperpropylalkine in solution in absolute ether. The picrate is a citron-yellow powder. The aurochloride,  $N(C_5H_{10})C_3H_6.OBz.HAuCl_4$ , forms a canary-yellow crystalline powder.

By the action of bromine on piperpropylalkine or its hydrobromide, there was obtained, not as was expected, a compound of the formula  $C_8H_{15}NBr_2$ , but a substance,  $C_8H_{17}NBr_2$ , crystallising in colourless rectangular tables and needles. As this compound is also obtained by heating piperpropylalkine hydrobromide with concentrated hydrobromic acid in sealed tubes at  $120^\circ$ , it most probably has the constitution  $N(C_5H_{10})(C_3H_6Br).HBr$ . By shaking with silver chloride, a crystalline chlorobromide is obtained, from which a crystalline aurochloride and platinochloride were prepared, and also a picrate crystallising in sparingly soluble needles.

A. J. G.

**Belladonine.** By G. MERLING (*Ber.*, **17**, 381—385).—The mixture of belladonine and atropine, of which commercial belladonine is composed, is boiled with baryta-water to decompose the atropine, when the belladonine,  $C_{17}H_{21}NO_2$ , remains as a brown resin. The auro- and platino-chlorides are insoluble in cold water. Belladonine is decomposed by boiling with baryta dissolved in a mixture of equal parts of alcohol and water, yielding tropine and an acid of the composition  $C_{10}H_{12}O_3$ , or probably a mixture of tropic, atropic, and isatropic acids.

The base oxytropine which Ladenburg obtained by boiling belladonine with alkalis exists ready formed as an impurity in crude belladonine.

W. C. W.

**Crystallised Colchicine.** By A. HOUDÈS (*Compt. rend.*, **98**, 1442 1444).—Three kilos. of colchicine seeds were exhausted with 100 kilos. of alcohol of  $96^\circ$ , the liquid filtered, the alcohol distilled off, and the residue treated repeatedly with a 5 per cent. solution of tartaric acid, which dissolves out the colchicine, but leaves fatty and resinous matters undissolved. The filtered solution was then agitated with chloroform, the chloroform removed by evaporation, and the crude product purified by repeated crystallisation from a mixture of equal parts of chloroform, alcohol, and benzene. The yield from the seeds is about 3 grams per kilo., whilst that from the bulbs is only 0.4 gram per kilo.

The colchicine thus obtained forms nodular groups of colourless prisms, slightly soluble in water, glycerol, and ether, but soluble in all proportions in alcohol, benzene, and chloroform. It has a very bitter taste, and an alkaline reaction, contains nitrogen, and burns without residue. It is hydrated, and melts at  $93^\circ$ , but after drying at  $100^\circ$ , the melting point rises to  $163^\circ$ . A solution of colchicine does not reduce an alkaline copper solution, but after prolonged boiling with dilute sulphuric acid, it reduces it immediately, and in this respect resembles solanine. Colchicine combines with certain

organic acids, but is decomposed when brought in contact with strong acids.

Concentrated or dilute inorganic acids dissolve colchicine and form a citron-yellow solution; nitric acid produces a transient violet coloration. Solutions of colchicine are precipitated by potash and soda, but not by ammonia. Tannin produces a white precipitate soluble on heating; platinum tetrachloride, an orange-yellow precipitate; an aqueous solution of iodine, a kermes-red precipitate; mercuric potassium iodide, a yellow precipitate; iodine in potassium iodide, a maroon-yellow precipitate.

Colchicine exerts a physiological effect only in relatively large doses. Respiration and the functions of the heart are considerably modified, and the general effect is a state of collapse, with stupor, but without insensibility.

C. H. B.

**Muscarine.** By J. BERLINERBLAU (*Ber.*, **17**, 1139—1145).—*Muscarine* can be prepared synthetically by the following process. Monochloroacetal obtained by Paterno and Mazzara's process (*Gazzetta*, **3**, 245) is heated with trimethylamine in sealed tubes at 130° for three or four days. The product is distilled in a current of steam, and the aqueous residue is digested with silver oxide to remove trimethylamine hydrochloride; the filtrate from this is then neutralised with hydrochloric acid, and the platinumchloride is prepared by fractional precipitation. The first precipitate consists of octahedra and the last portion of rhombic plates. The latter have the composition  $(\text{NMe}_3\text{Cl} \cdot \text{CH}_2\text{CH}(\text{OEt})_2)_2\text{PtCl}_4$ , i.e., the platinumchloride of the ethylic salt of muscarine. The octahedral crystals have the composition of muscarine platinumchloride,  $(\text{NMe}_3\text{Cl} \cdot \text{CH}_2\text{COH})_2\text{PtCl}_4$ . The base obtained from this salt was identified as muscarine by its physiological action on the heart.

W. C. W.

**Putrefaction Alkaloids.** By L. BRIEGER (*Ber.*, **17**, 1137—1139).—In the putrefaction of flesh, choline is converted into the more poisonous neurine. A subcutaneous injection of 0.04 gram of neurine hydrochloride is fatal to a rabbit weighing 1 kilo., but at least 0.5 gram of choline hydrochloride is required to produce a similar effect.

W. C. W.

**Putrefaction Alkaloids.** By Z. MARINO-ZUCCO (*Ber.*, **17**, 1043—1044).—The author has shown (*Abstr.*, 1884, 343) that Selmi's ptomaine is neurine, and states that he is continuing his investigation of the physiological action of neurine.

A. B.

**Changes which Proteid Matters undergo by the Action of Pancreatic Ferment.** By J. G. OTTO (*Zeit. Physiol. Chem.*, **8**, 129—148).—Well washed and finely mixed fibrin was digested with a watery solution of ox pancreas at the temperature of the room, any putrefactive changes being prevented by the addition of ether. The first decomposition-product, globulin, was separated by saturating the filtered fluid with magnesium sulphate. The coagulating point of the purified globulin dissolved in weak sodium chloride was 70—



75. Dried at  $110^{\circ}$  C. the globulin gave the following percentage composition: 0.55—0.73 ash; 53.17 C; 7.29 H; 15.8 N; 1.17 S. These numbers agree so closely with those Hammarsten found for serum-globulin that the two bodies may be considered identical; the specific rotatory power also is  $-48.1$ , which is very similar to the  $-47.8$  Fredericq found for serum-globulin.

After removal of the globulin, the propeptone (hemialbumose) can be obtained by saturating with common salt, and adding hydrochloric acid: the purified propeptone also agrees in its chemical composition with the gastric propeptone. Both, in solution or when exposed to damp, are converted partly into a coagulable albumin.

In order to obtain the peptone, it is best to first remove the globulin and propeptone by boiling with sodium acetate and ferric chloride after slightly acidifying with acetic acid, filtering off the precipitate, and then separating the peptone with phosphotungstic acid, after the addition of  $\frac{1}{3}$  the volume of strong sulphuric acid. This precipitate is decomposed with caustic baryta, and baryta-water added until the whole is distinctly alkaline, the excess afterwards removed from the filtrate by passing carbonic anhydride through the solution. The percentage composition of the pure peptone is as follows: 0.3—0.6 per cent. ash; 50.0 C; 6.81 H; 15.83 N; 1.06 S. Kossel's analysis of gastric peptone agrees very closely with this; the specific rotatory power is  $65.2-66$ ; that of gastric peptone, according to Hoffmeister, being  $63.5$ .

The author finds, as Kühne did, that a large proportion of the peptone formed by tryptic digestion is converted into anti-peptone when submitted to further digestion.

J. P. L.

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## Physiological Chemistry.

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**Respiration of Air charged with Petroleum Vapour.** By POINCARÉ (*J. Pharm.* [5], 7, 290—291).—The author has kept animals continuously in an atmosphere which was frequently charged with the vapour of petroleum. The effects observed were principally greater frequency and amplitude of the respiratory movements, a diminution of the cardiac movements, and a greater intensity of the beating of the heart. This was accompanied by cutaneous irritation, and a general tendency to sleep and languor. Guinea-pigs finally succumbed under the treatment. The autopsy showed general congestion. Workmen engaged in the distillation of petroleum complain of heaviness in the head and great irritation of the mucous membrane of the nose. W. R. D.

**Source of Hippuric Acid in the Urine.** By C. SCHOTTEN (*Zeit. Physiol. Chem.*, 8, 60—69).—E. and H. Salkowski, after they

obtained phenylpropionic acid from sepsis of proteid matter, showed that in the living organism this was converted into benzoic acid, which, combining with glycocholl, formed hippuric acid.

The author supposes  $\alpha$ -amidophenylpropionic acid to be a second source. To test the correctness of this view 0.7 gram of the acid was given to a dog fed for some time previously on a meat diet; from the urine only 0.01 gram hippuric acid was obtained. It cannot therefore be considered as a source.

Amidophenylacetic acid is converted into mandelic acid under similar conditions. Mandelic acid is not converted into hippuric acid as asserted in many text-books, but appears unchanged in the urine.

J. P. L.

**Occurrence of Glycerolphosphoric Acid in Urine.** By L. EYMONNET (*J. Pharm.* [5], 7, 134—138).—The glycerolphosphoric acid in the urine was estimated by taking advantage of the fact that it is not precipitated by the ordinary reagents for phosphates; the latter were removed from 200 c.c. of urine by magnesia mixture, and the filtered liquid evaporated to dryness, and ignited with potassium nitrate. The residue was extracted with dilute nitric acid, and the solution, after concentration, was precipitated by ammonium molybdate in the ordinary way. It is seen from the results that in the case of dogs during starvation less glycerolphosphoric acid is excreted by the urine than during the normal condition. When injected into the peritoneum as calcium glycerolphosphate, it is nearly all oxidised before being excreted by the urine, but when injected into the veins an appreciable increase in the quantity of glycerolphosphoric acid excreted by the urine is observed. A notable increase in the quantity of glycerolphosphoric acid is found in the urine of phthisical patients having abnormally fatty livers, while the liver contains much lecithin; in the case of one patient, as much as 3.38 per cent. was isolated from the fresh liver.

W. R. D.

**Elimination of Hypophosphites by the Urine.** By L. EYMONNET (*J. Pharm.* [5], 7, 138—140).—By injecting sodium hypophosphite into the veins of dogs, and estimating the total phosphates and unaltered hypophosphite in the urine, the author shows that the elimination of the dose is complete in about 24 hours; part of the hypophosphite is found in the urine as phosphate, and the remainder as unaltered hypophosphite, yet the quantity oxidised appears to increase in proportion to the quantity of hypophosphite administered.

W. R. D.

**Knowledge of Indigo-forming Substances in the Urine.** By J. HOPPE-SEYLER (*Zeit. Physiol. Chem.*, 8, 79—84).—From 25 litres of normal dogs' urine, the author obtained 1 gram of crystallised indican, and about 0.5 gram of pure phenylsulphate of potassium = 0.002 gram per cent. Indican exists in dogs' urine in sufficient quantity to be detected by Jaffe's reaction.

In order to determine whether indican underwent any change in the organism, 2.7 grams were injected into an animal; in the urine indican only was found.

Neither orthonitrocinnamic acid, orthoamidocinnamic, or ortho-nitrobenzaldehyde alone or with acetone produced any increase in the quantity of indican. J. P. L.

**Extraction of Indigotin and Indirubin from Urine.**—By A. C. MÉHU (*J. Pharm.* [5], 7, 122—126).—The author has previously shown that certain colouring matters of both normal and pathological urine may be extracted by rendering the urine acid with sulphuric acid, and then adding ammonium sulphate to saturation: this method can be applied to the isolation of the indigotin and indirubin from violet or blue urine. The urine is rendered strongly acid with sulphuric acid, about 1 gram of sulphuric acid being added to 1 kilo. of urine, and then saturated with anhydrous ammonium sulphate. In this way, a mixture of indigotin and indirubin, the blue and red colouring matters of violet urine, is precipitated. These substances may be separated, as the author has previously shown, by 50 per cent. alcohol, which, in the cold, dissolves the indirubin almost exclusively. The insoluble indigotin is purified by washing with water and spontaneously drying. Indigotin is very readily soluble in hot phenol, and as the liquid cools the greater part of the indigotin is deposited in well-defined crystals. An approximate estimation of indigotin may be made by a colorimetric process, using a standard solution of indigotin in phenol to which absolute alcohol or glycerol has been added to prevent solidification. The author has determined the solubility of indigotin from indigo in various liquids. Boiling creosote (from beechwood) is a good solvent of indigotin; the solution deposits the substance in crystals as it cools. Oils of bitter almonds, turpentine, gaultheria, rosemary and amyl alcohol are also solvents of indigotin. The indigotin from violet urine is likewise soluble in oils of anise, bitter almonds, and gaultheria, forming violet solutions, but the indigotin from the two sources appears to differ when boiled with anise or oil of winter green; the indigotin from indigo is unaffected to any appreciable extent, but the indigotin from urine is decolorised. W. R. D.

**A Urinary Pigment.** By P. PLÓSZ (*Zeit. Physiol. Chem.*, 8, 85—94).—When urine is boiled for some time with hydrochloric acid, a complete change occurs in the colour, indigo frequently separating out after 20 minutes. On shaking the coloured urine with ether, a red colouring matter is obtained (mixed with small quantities of benzoic acid and urobilin), to which the author has given the name of urorubin. To purify this colouring matter, the residue, after distilling off the ether, is washed several times with hot water to remove benzoic acid and some yellow colouring substances (urobilin, &c.). The residue is again dissolved in ether, and shaken with weak soda-ley to remove the last traces of urobilin. By very careful evaporation of the ethereal or alcoholic solution, urorubin can be obtained in crystalline plates; it is insoluble in water, soluble in alcohol, chloroform, and especially in ether, imparting to the solutions a garnet colour.

Strong hydrochloric and sulphuric acids slowly dissolve and de-

colorise it, nitric acid and alkalis more rapidly. Urorubin probably owes its origin, like indican, to sepsis in the intestine. It is formed both in acid and alkaline urine.

The urine thoroughly exhausted with ether is still of a dark colour; this can be completely removed by exhausting with amylic alcohol. The colouring matter obtained by evaporating this alcoholic solution is identical with Heller's urrhodine and Thudichum's uromelanin. From a day's urine, the author obtained 5—6 grams uromelanin.

J. P. L.

**Chemical Constituents of the Thyroid Gland of Men and Oxen.** By N. A. BUBNOW (*Zeit. Physiol. Chem.*, **8**, 1—47).—The first 30 pages contain a complete *résumé* of the previous literature on the subject.

The author makes extracts of the fresh gland (freed from fat, &c.), with water, 10 per cent. NaCl solution, and 0·1 per cent. KHO solution, and gives in full their general reactions. From a watery extract, he obtained xanthine, hypoxanthine, and lactic acid, but no guanine. He has also analysed the soluble proteïds which he obtained by precipitating with acetic acid and purified by washing with distilled water, alcohol, and ether; the general result is that whether human or ox gland be taken the composition of the proteïd is identical: the proteïd obtained from the 10 per cent. NaCl extract and 0·1 per cent. KHO extract was higher in carbon but lower in nitrogen than that obtained from an extract of 0·1 per cent. KHO after long digestion.

J. P. L.

**Composition of a Pathological Liquid.** By J. REGNAULD and VILLEJEAN (*J. Pharm.* [5], **7**, 201—209).—This paper contains a physiological and chemical description of a liquid obtained from an inguino-abdominal tumour. The following is an abstract of the more important chemical features of the liquid. The total quantity obtained was about 260 grams; it had an oily consistence, an amber colour, and contained suspended particles. By filtration, a perfectly clear alkaline liquid was obtained which had a sp. gr. of 1·038 at 13°. When this liquid was merely mixed with water coagulation occurred, and the mixture became nearly solid. By agitating with water the mixture again became clear, with the exception of a few flocks that still remained insoluble. When microscopically examined, the coagulum appeared to be identical with the fibrin of blood and of lymph. The flocks which remained after agitation with water, when similarly examined, appeared to be identical with the fibrin of plasma. The following table represents the results of a chemical analysis of the liquid. 100 grams contained :

Water .....	87·612
Fibrin .....	1·860
Metalbumin .....	6·240
Serin.....	2·460
Mucin .....	none
Peptones, &c. ....	0·993
Chlorides (K and Na).....	0·542

Carbonates, sulphates, and phosphates of alkalis and alkaline earths .....	} 0.293

W. R. D.

**Physiological Action of Borax.** By F. VIGIER (*J. Pharm.* [5], 7, 301—310).—From experiments on dogs and men, the author concludes that borax has no injurious physiological action even when given in large doses. Thus 3.5 grams of borax were taken on an empty stomach; salivation became rather more copious, and the saliva was found to be more than normally alkaline, the appetite was increased. With dogs, a solution of borax was injected in the veins. doses of 1.25 gram in 5 c.c. of water being given at intervals of half an hour until 5 grams had been given. Borax was subsequently found in the saliva as well as in the urine, in fact it appears to be slowly eliminated from the system by the latter excretion. In order to detect the borax in these cases, large quantities of the urine and saliva were evaporated, and after acidifying with hydrochloric acid the flame spectrum of the liquid was examined. The ordinary tests for borates are not sufficiently delicate, and the usual flame reaction for boric acid is masked by the presence of organic matter and sodium salts.

W. R. D.

**Transformation of Nitriles in the Organism.** By P. GIACOSA (*Zeit. Physiol. Chem.*, 8, 95—113).—Benzonitrile enclosed in gelatine capsules and given with food to a dog, is eliminated partly by the lungs, fæces, and urine. The odour of benzonitrile in the respired air was very persistent, lasting six days after a dose of 2.4 grams. It acts as a poison, producing convulsions, has a local action on the mucous membrane of the stomach, sometimes producing large ulcers. In large doses, it paralyzes respiration and death ensues. Neither benzoic, hippuric, nor any hydroxy-acids were found in the urine. The ratio between the mineral and combined acids is considerably altered; before the experiment, the ratio was nine of mineral to one of combined,  $\frac{A}{B} = \frac{9}{1}$ ; after,  $\frac{A}{B} = \frac{0.120}{1}$ : the total quantity of sulphates too was diminished; before the experiment, it was about 0.390 gram per day, after, 0.117 gram.

Phenylacetoneitrile acts as a very violent poison, does not give rise to any odour either in the expired air or urine, the urine is strongly acid, sometimes contains albumin, and so rich in urates and uric acid as to have a creamy consistency. Phenaceturic acid was obtained from the urine, which differs from E. and H. Salkowski's acid obtained from phenylacetic acid in having a higher melting point (Salkowski's 143°, Giacosa's 185—186°). Acetonitrile is the least poisonous; when given to a dog, part is excreted as acetic acid; after a dose of 4 grams, 0.25 gram of acetic acid was found in the urine.

Propionitrile produces violent vomiting and is very poisonous; part is eliminated unchanged by the lungs, and about one-tenth as propionic acid in the urine.

During the whole period the animals were under the influence of the nitriles, the author observed in every case (even when the urine was very acid) crystals of ammonium magnesium phosphate in large quantities; as they appear normally only in alkaline urine, it is probable the acid in the urine after feeding with acetonitrile is not acetic. The author intends to further investigate this.

J. P. L.

**Fate of Iodoform and Chloroform in the Organism.** By A. ZELLER (*Zeit. Physiol. Chem.*, 8, 70—78).—The author has previously shown that iodoform, when applied to the abdominal cavity, may produce fatal results; as excretion is much slower than absorption, a consequent retention of iodine occurs in the blood and tissues. According to Hügys, the absorption is due to the decomposition of the iodoform and formation of a compound of iodine and albumin. The author's experiments support this view. 300 grams of an albumin solution containing 2.51 grams of iodine were given to a dog; the excretion of iodine lasted nine days, 1.626 gram being accounted for; only a very small part passes through unchanged in the faeces.

When chloroform is used as an anæsthetic, part is found after a few hours in the urine. Nothnagel found, after subcutaneous injection, bile pigments present. Kappeler, on the other hand, could not find any in 25 different cases. The present paper chiefly relates to the amount of chloroform eliminated as chloride in the urine. A dog fed on 500 grams meat daily was given in the first experiment 7 grams, in a second 9 grams chloroform, enclosed in capsules. The increase of chlorides in the first case lasted four days; in the second eight days. In the second experiment the increase amounted to 5.71 grams Cl, corresponding with 6.41 grams chloroform; consequently about one-third is exhaled by the lungs.

J. P. L.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Schizomycetic Fermentation. Part IX.** By A. FITZ (*Ber.*, **17**, 1189—1196).—In addition to Pasteur's butyric acid ferment and the micrococcus previously described by the author, a third variety of schizomycetes exists, which ferments calcium lactate to butyric acid. It is cylindrical in form, its dimensions being 0·7—1 micromm. broad and 1·8—2·4 long; cultivation in a vacuum diminishes the length, whilst the presence of free acid increases the dimensions to 1·5 micromm. in breadth, and to 7—8 in length. Not only the developed ferment but also its germs are destroyed by exposure to a temperature of 58°. The following substances undergo fermentation when brought in contact with this variety of schizomycetes; grape-sugar, cane-sugar, milk-sugar, mannitol, calcium lactate, malate, tartrate, and citrate, and also glycerol and calcium glycerate with difficulty. Ery-



throl, dulcitol, and quercitol are not fermented by it. In the fermentation of calcium lactate, not only butyric but also propionic acid are produced; calcium tartrate on the other hand yields succinic and acetic acids.

The author denies the statement made by Hueppe, Koch, Gaffky and Löffler, that liquids heated in a steam chamber acquire the temperature of the surrounding vapour but very slowly. He also reiterates his statement which has been denied by Duclaux that *Mucor racemosus* inverts cane-sugar.

W. C. W.

**Butyric Fermentation excited by Garden-soil.** By P. P. DEHÉRAIN and L. MAQUENNE (*Ann. Agronomiques*, 10, 5—9).—The authors have continued their inquiry into the products formed during the fermentation of solutions of sugar by soil bacteria. By employing 30 litres of water, 1 kilo. each of sugar and chalk, and 1 kilo. of soil, and keeping the temperature at 35°, a very energetic fermentation was produced, a large quantity of gas evolved (consisting of hydrogen with a little carbonic anhydride), and in a month the sugar had entirely disappeared, and the liquid was acid. The organism producing these changes was a very active elongated bacillus, coloured blue by iodine, and resembling *Bacillus amylobacter*. The volatile products obtained by distilling 20 litres of the liquid consisted of about 10 c.c. ethyl alcohol, 4 or 5 c.c. amyl alcohol, and a small quantity of other alcohols boiling above 140°. The lime salts produced by the fermentation were converted into ethyl salts by distillation with sulphuric acid and alcohol, and furnished about 100 c.c. acetic ether (distilling 70—79°), 25 c.c. of an ether boiling 95—102°, and furnishing an acid which was probably propionic acid, and 100 c.c. of butyric ether distilling over between 115 and 122°. The total acids in the fermented liquid were estimated as equivalent to 247 grams sulphuric acid, corresponding with 450 grams of a mixture of equal parts of acetic and butyric acids. About half the sugar employed was thus converted into these acids. It is possible that the alcohols formed were due to the coexistence of the alcoholic fermentation with the butyric. The butyric bacillus of Fitz (*Bull. Soc. Chim.*, 38, 584) furnishes no acetic acid, and the author considers the bacilli acting in the two cases to be different.

J. M. H. M.

**Development of Starch-transforming Ferments in the Cells of the Higher Plants.** By W. DETMER (*Ann. Agronomiques*, 10, 45—46; from *Botan. Zeitung*, 1883, 601).—Ungerminated grains of wheat contain a little diastatic ferment, the quantity of which rapidly increases when the grains germinate in presence of oxygen. When the grain, after being soaked in boiled water, is placed in an atmosphere of hydrogen, germination still takes place to a small extent by means of intramolecular respiration; but in this case diastase is not developed, even if a little free acid (citric), which favours the production of diastase, is added. Oxygen, therefore, is necessary to the formation of diastase in the cells of the higher plants.

J. M. H. M.

4 c 2

**Part played by Vegetable Acids in causing the Turgescence of Cells.** By H. DE VRIES (*Ann. Agronomiques*, 10, 139—141; from *Botan. Zeitung*, 1883, 849).—The turgescence of cells is to a large extent caused by the osmotic action between the crystallisable substances contained in the cell sap and the watery liquid by which the cells are surrounded. The outward pressure thus produced is very considerable, and has been estimated by Pfeffer to amount to as much as 7 atmospheres in the articulation of a bean leaf and 13 atmospheres in the pith of a sunflower stem. If increasing quantities of crystalloids be added to the water surrounding a living cell, the turgescence of the cell is progressively diminished, until finally the tension of the enclosed protoplasmic sac becomes nil, and the sac contracts, loses water, and detaches itself from the cell-wall. The author applies the term "plasmolysis" to this phenomenon, and has determined the strength of various solutions of crystalloids required to bring it about in the cells of different plants. With the red beet, for example, solutions of the following strengths are necessary:—Cane-sugar, 27—28 per cent.; magnesium sulphate, 26—28 per cent.; sodium sulphate, 17—18 per cent.; sodium or potassium nitrate, 6—7 per cent.; potassium chloride, 4—5 per cent.; sodium chloride, 3—4 per cent. The author believes a considerable portion of the turgescence to be produced by the vegetable acids and their compounds with mineral and organic bases, especially in the cells of young tissue. He finds that the salts of vegetable acids with inorganic bases produce 21—27 per cent. of the turgescence in the cells of the petioles of *Heracleum pubescens*, 30 per cent. in the summits of *Carum carui*, 35 per cent. in the cells of *Delphinium azureum*. Salts of vegetable acids with organic bases furnish 11 per cent. of the turgescence in monkshood, 16 per cent. in young petioles of *Rheum hybridum*, 19 per cent. in the epicotyledonous internode of a young haricot. The effect of free oxalic acid is shown in the following table:—

	Per cent. of total turgescence.		
	Rheum officinale.	Rheum hybridum.	Begonia rex.
Free oxalic acid.....	16	42	29·2
Potassium hydrogen oxalate ..	18	17·7	14·2
Calcium and magnesiumoxalates	3·5	2·6	4·2
	37·5	62·3	47·6

A molecule of glucose, by furnishing 3 mols. of oxalic acid, triples its power of causing turgescence; when converted into malic acid, the augmentation is a half less. Glucose is the commonest and most important of the soluble matters causing turgescence, contributing for example 50—60 per cent. of the total effect in young petioles of *Heracleum spondylium*, and 80 per cent. in petioles of the rose. Inorganic salts do not occur in large quantities in young tissues, but certain plants accumulate them, *e.g.*, in the summits of the artichoke, potassium nitrate produces 40 per cent. of the turgescence, and in the young petioles of *Gunnera scabra* potassium chloride produces 52—

56 per cent. Potassium, on combining with an acid, increases the force of turgescence, whilst lime does not. A molecule of potassium malate, for example, has twice the osmotic force of malic acid or of calcium malate. Hence the accumulation of potassium salts in young tissues which have most need of turgescence, and their gradual replacement by calcium salts as the tissues grow older.

J. M. H. M.

**Attraction between Soluble Substances in Dilute Solutions and Water.** By H. DE VRIES (*Ann. Agronomiques*, 10, 141—143).—The author measures the attraction of a dissolved substance for water by the power which its solution possesses of removing water from the protoplasmic contents of vegetable cells. The degree of concentration necessary to produce “plasmolysis” or the contraction and separation of the cell-contents from the cell-wall may be observed, or the following method may be adopted:—When the apex of a growing shoot is divided by longitudinal cuts into four filaments, these filaments become curved outwards by the tension of their component cells. If the curved ends be immersed in pure water, the curvature increases; in strong solutions of soluble substances it is lessened; and in solutions of a certain strength no alteration of the curve is produced. Solutions of various substances of such strength as to behave in the manner last mentioned are called *isotonic*, and the strength of the solution is inversely proportional to the attraction of the dissolved substances for water. *Isotonic coefficients* express the affinity for water of 1 mol. of various substances, that of a  $\frac{1}{2}$  mol. of oxalic acid being taken as unity:—

Cane-sugar .....	1·9	Potassium or sodium nitrate,	
Inverted sugar.....	1·9	potassium, sodium, or am-	
Malic acid.....	2·0	monium chloride, potas-	
Tartaric acid.....	2·0	sium acetate, monopotas-	
Citric acid.....	2·0	sium citrate.....	3·9
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Tripotassium citrate.	5·0	Magnesium malate .....	1·9
		„ sulphate .....	2·0
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Potassium oxalate or sulphate.....	3·0		
„ phosphate or tartrate.....	4·0		
„ malate or dipotassium nitrate.	4·1		
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Magnesium citrate.....	3·9		
„ chloride .....	4·3		
Calcium chloride.....	4·3		

Organic substances have thus a coefficient of 2; alkaline salts with 1 atom of metal, 3; with 2 atoms of metal, 4; with 3 atoms of metal, 5; salts of the alkaline earths derived from 1 mol. of acid, 2; from 2 mols. of acid, 4. The isotonic coefficient of a salt is the sum of the coefficients of its acid and base, these being—acids, 2; alkali metals, 1; metals of the alkaline earths, 0.

J. M. H. M.

**Methods of Studying the Influence of Light on the Respiration of Plants.** By G. BORNIER and L. MANGIN (*Ann. Agronomiques*, 10, 40—41; from *Bull. Soc. Bot. de France*, 30, 235).—The authors have verified the conclusion arrived at by a different method, that light retards respiration, by actually measuring by means of standard baryta-water the carbonic anhydride produced in a given time by plants destitute of chlorophyll. J. M. H. M.

**Influence of Light on the Disengagement of Oxygen by Plants.** By J. REINKE (*Ann. Agronomiques*, 10, 38—40, and 136—137; from *Botan. Zeitung*, 1883, Nos. 42, 43, 44).—The author describes the means adopted by him to measure the oxygen disengaged by leaves in presence of light of varying intensity, by counting the bubbles of gas which escape from a given leaf surface of an aquatic plant in measured intervals of time. *Elodea*, having very thin leaves, is especially suitable. The light of the sun is reflected from a heliostat through a convex lens into a darkened chamber. The intensity of light to which the leaf is subjected then varies according to its position in the double cone of rays formed by the lens. Working in this way the author finds that the disengagement of oxygen attains its maximum with light of normal intensity (*i.e.*, at twice the focal distance of the lens, where the diameter of the cone of rays is the same as that of the lens), that it diminishes rapidly, with intensities of  $\frac{1}{4}$ ,  $\frac{1}{8}$ ,  $\frac{1}{16}$ ; but on the other hand remains almost constant when the intensity is 2, 4, and 8 times the normal.

The author has adopted his method of counting the number of bubbles of gas escaping from a given leaf surface of an aquatic plant (*Elodea*) in a given time to the study of the influence of light of different colours on the disengagement of oxygen by plants. The same apparatus was employed as that previously described with the interposition of a prism of known dispersive power adjusted for the minimum angle of deviation, in the path of the conical beam. The spectrum was received on a screen, composed of two vertical plates of wood, adjustable at any distance from each other. The band of coloured light passing between the wooden uprights was concentrated on the leaf by a lens, the distance between the uprights being so adjusted for each colour as to obtain an equal luminous concentration (*i.e.*, an equal number of wavelengths) in all cases. The maximum disengagement of oxygen corresponds with the maximum absorption of chlorophyll, and is situated in the red, not far from the line B; the curve descends rapidly towards the ultra-red, more slowly towards the ultra-violet, but, contrary to the experiments of Engelmann, there is no augmentation in the disengagement of oxygen, corresponding with the absorption-band commencing between the lines b and F, and extending over the whole of the right side of the spectrum. J. M. H. M.

**Structure and Functions of the Epidermic System of Plants.** By WESTERMAYER (*Ann. Agronomiques*, 10, 37—38).—In this paper, the author insists on the importance of the epidermic layers of cells as reservoirs of water. Sometimes these cells contain more water than

all the other tissues of the plant together, and in some cases the cell-walls are arranged in folds like a venetian blind, so that the volume is subject to much variation. The same rôle is played by the cells of the hypodermis, also destitute of chlorophyll, but, unlike the epidermic cells, originating from the periblem. When a leaf fades, these expansible cells of the epidermis and hypodermis are the first to give up their water, at the same time contracting in volume. The water of the epidermic cells absorbs the obscure heat of the sun's rays, and in Dehérain's experiments on the action of the electric light on vegetation these cells were the only ones injuriously affected (blackened).

J. M. H. M.

**Contributions to the Doctrine of Thermic Constants in Plants.** By STAUB (*Ann. Agronomiques*, 10, 42—43; from *Botan. Jahrb.*, 3, 131).—The thermal constant of a plant, according to Oettinger, is the sum of the mean temperatures of the days of active vegetation from the commencement of growth to some definite phase in the plant's life, minus a certain initial temperature (*seuil*), different for different species, and determined by comparing the observations of successive years. The author objects to this, that the development of a plant depends not only on the aggregate quantity of heat which it receives, but above all on the temperature during growth, which cannot be expressed by adding together thermometric measurements.

J. M. H. M.

**Means of Protecting Plants against Frost.** By H. R. GOPPERT (*Ann. Agronomiques*, 10, 41—42).—Sachs maintains that plants, bulbs, and roots are killed, not by being frozen, but by too sudden and rapid thawing. The author, on the other hand, by submitting narcissus, tulip, and hyacinth bulbs and potatoes to a temperature of  $1.4^{\circ}$  below zero, and then dividing them into two lots, one being suddenly cooled to  $-8^{\circ}$ , and the other plunged in water of  $1^{\circ}$ , found that the temperature of  $-8^{\circ}$  killed all the bulbs, whether the subsequent thawing was slow or rapid, but that none of the bulbs cooled to  $-1.4^{\circ}$  suffered any damage, the potatoes only being frozen. By experimenting with the flowers of the exotic orchids *Pajus* and *Calanthe*, which become blue by development of indigo as soon as they die, he also shows that death occurs when the flowers are frozen, and consequently that no amount of care bestowed on the thawing of frozen plants is of any avail if the frost has been sufficiently severe. The buds of some ligneous plants were found to stand freezing at  $-16^{\circ}$  to  $-20^{\circ}$ , and subsequent thawing at  $25^{\circ}$  without damage.

J. M. H. M.

**Contents of the Cribriform Vessels of "Cucurbita Pepo."** By E. ZACHARIAS (*Ann. Agronomiques*, 10, 138—139; from *Botan. Zeitung*, 1884, 65—73).—When a pumpkin is cut across, there exudes from each bundle of vessels a drop of liquid having an alkaline reaction; after a few hours the drop solidifies into an elastic mass. The author has collected a sufficient number of drops in a watch-glass to recognise the presence of an albuminoid similar to fibrin, dextrin, potassium phosphate, magnesium salts, nitrites, and nitrates. The alkaline reaction is ascribed to potassium phosphate. The

albuminoïd is deposited, on standing, in the form of mucilaginous threads, the separation of which is prevented by 0·2 per cent. hydrochloric acid, and by very dilute potash, but not by 10 per cent. sodium sulphate solution. Strong potash causes an immediate precipitate of white flocks, soluble in excess of water. Alcohol transforms the mucilage into a hard white opaque mass, coloured yellow by nitric acid. Copper sulphate and potash give a violet solution; ferrocyanide of potassium and ferric chloride both colour the mucilage deep blue. The mucilage is soluble in gastric juice and very dilute potash; strong potash hardens it and renders it opaque; 0·2 per cent. hydrochloric acid and 10 per cent. soda cause it to swell without dissolving; sodium chloride is without action.

J. M. H. M.

**Mascate Pea.** By A. RICHE and A. RÉMONT (*J. Pharm. Chim.* [5], 7, 29—32).—The seed commonly known as the mascate pea is yielded by a plant largely found in Brazil, belonging to the genus *Canavalia*, of the natural order *Papilionaceæ*. It was believed that the seeds, which are about the size of small kidney beans, could be used as a substitute for coffee. A chemical examination by the author negated the supposition, for they were found to contain no caffeine. Experiments were then made with the roasted seeds to discover whether they could be used in the place of chicory or other roasted beans, for mixing with coffee. These experiments indicated that the canavalia seeds after roasting contain less matter soluble in water than chicory, roasted acorns, or barley, and that the aqueous solution has much less colouring power, but contains more nitrogenous matter, than the aqueous solutions of the other substances. The authors consider that as these seeds are comparatively rich in albuminoïds (5—6 per cent.), their use for mixing with coffee should be encouraged.

W. R. D.

**Results obtained from Experimental Plots at Grignon in 1883.** By P. P. DEHÉRAIN, BOREAU, and MARCHAL (*Ann. Agronomiques*, 10, 97—112).—The season of 1883 was characterised by great equality of temperature and a large and pretty equally distributed rainfall. The hot weather of June was favourable to the ripening of wheat, and the crop would have been generally good but for the extremely wet autumn of 1882, which hindered sowing. Oats everywhere yielded unusually large crops, and the grass and forage crops were extremely abundant, being favoured by a warm moist summer. The hot and dry August exercised a favourable influence on the quality of the sugar-beet crop and its richness in sugar, but the warm and mild September which followed produced some amount of deterioration. The disposition of the plots in the ninth year of experiment (1883) was altered, so as to include experiments on rotations, on applications of the manures which the eight preceding years have shown to be most suitable to the soil, and on laying down land with permanent pasture.

*Wheat.*—The same plots carried this crop for the fourth successive year (1883), and none of them had received any manure since 1881 at latest, the purpose being to ascertain the unexhausted effect of

manures previously applied. In May, 1883, however, the plant appeared so poor over all the plots that it was considered advisable to top-dress half of them with nitrate of soda, but this application, made so late in the season, produced no beneficial result. The influence of the manures applied in previous years, although much lessened, is still sensible, the continuously unmanured plot producing only 14·6 hectolitres of grain per hectare, whilst the average yield of all the plots was 17·5 hectolitres. Farmyard manure ploughed in (1875—1879) continues to show much better results than when spread on the surface. Nitrate of soda, four years after application, still exerts an appreciable influence on the yield. Sulphate of ammonia still remains inferior to nitrate of soda, and Plot 32, which received a very heavy dressing (1200 kilos.) of sulphate of ammonia for three years (1875—1878) has not yet recovered the injury it received, and gives the worst yield of any plot save continuously unmanured ones. The decreasing effect of the residues of previous manuring is shown in the following table, which gives the yield of grain in quintals per hectare for each year since the application of manure was discontinued.

	1880.	1881.	1882.	1883.	Mean. 1880-83.
Unmanured .....	25·00	16·40	21·90	11·70	18·75
Farmyard manure ploughed in ..	34·06	23·92	23·44	17·42	24·71
"          "          spread .....	27·00	16·00	20·00	15·00	19·50
Nitrate of soda .....	27·75	21·00	21·50	14·00	21·06
Sulphate of ammonia .....	23·30	18·60	20·00	13·50	19·95
Blood manure (Souffrice's) .....	34·00	21·60	23·00	14·00	23·15
Leather manure (Coignet's) ....	26·00	23·20	20·00	13·00	20·5
Mean of all the plots .....	28·53	21·00	21·07	14·07	21·1

The percentage of nitrogen found in 1883 in three plots was 0·169, identical with the figure obtained in 1881; the authors attribute this conservation of nitrogen to the free growth of weeds, which are very difficult to keep down when so many corn crops are taken in succession.

*Oats*, after having been grown for eight successive years on the same plots, were in 1883 transferred to plots some of which had grown green maize for the seven preceding years, and the rest for six years with beet in 1882. On all these plots, very fine crops of oats were obtained, the continuously unmanured plot yielding 51·2 hectolitres of grain per hectare, the highest yield being 80 hectolitres from a plot which received heavy dressings of farmyard manure in 1875—1882 but nothing in 1883. On the soil of Grignon, no mixture of artificial manures gives such heavy crops as farmyard manure. Comparing the heavy crop of oats obtained in 1883 (even on the unmanured plot) with the poor yield of 1882, and with the wretched crops of wheat of 1883, the authors conclude that the chief reason for the striking improvement in the yield of oats is the fact that they have

this time followed the maize crop instead of being grown again consecutively, thus allowing of a thorough cleaning of the land.

*Beet* in 1883 was grown upon the plots which carried oats since 1875. The best results were obtained by farmyard manure with the addition of nitrate of soda. Flesh manure (Souffrice's) gave a slightly heavier crop, but the increase was not equal to the increased cost of the manure. The greatest percentage of sugar in the roots was obtained on the continuously unmanured plot, but the greatest total weight of sugar per acre was on the plot dressed with farmyard manure and nitrate of soda.

*Maize cut for fodder* was also transferred to the plots which had been in oats since 1875. The unmanured plot yielded the very fair crop of 64,000 kilos. per hectare, whilst the plot which received the heaviest dressing of farmyard manure yielded 92,000 kilos. The effect of previous dressings of farmyard manure was very marked. Chloride of potassium produced a considerable increase, although potash salts do not usually benefit other crops grown on the soil of Grignon.

*Sainfoin*.—The sainfoin sown in 1882 on the plots which had already carried it for three years, yielded in 1882 a medium crop, in which sainfoin predominated; in 1883, however, the sainfoin was in great part replaced by adventitious grasses, so that the original intention of keeping the plots under this crop has been abandoned, and they will go into mixed seeds. The heaviest crops in 1883 were obtained on the plots which had received sulphate of ammonia or nitrate of soda in previous years.

J. M. H. M.

**Farmyard Manure.** By A. B. GRIFFITHS (*Chem. News*, **49**, 279—280).—The author has observed that the watery extract of farmyard manure is a very favourable medium for the production, multiplication, and sustenance of bacteria, bacilli, vibrios, &c. These organisms, along with their germs, may be completely destroyed by a solution either of ferrous sulphate, containing at least 0.0269 gram per 100 grams of water, or copper sulphate (0.0073 per 100), or of sodium chloride (5 per 100). Moreover, it is shown that the potato parasite, *Peronospora infestans*, can thrive in farmyard manure, at least as regards the unlimited production of hyphæ without any further development. This, as well as the presence of seeds of weeds in this manure, is urged as evidence against its use on arable land.

D. A. L.

**Loss of Nitrogen during the Fermentation of Manures.** By H. JOULIE (*Compt. rend.*, **98**, 1444—1445).—During the prolonged fermentation of manure, there is a loss of nitrogen which may amount to more than 20 per cent., this loss being due entirely to the decomposition of the ammonia contained in the drainage from the manure. A certain proportion of the ammonia combines with the organic matter during fermentation, the amount thus fixed depending on the relative proportions of organic matter and ammoniacal nitrogen. The loss of ammonia is not affected by the addition of calcium phosphate, but is largely increased by the addition of calcium carbonate or sulphate.

C. H. B.



**Action of Superphosphates.** By P. WAGNER (*Dingl. polyt. J.*, 252, 303).—The author states that the degree of fineness of a manure is of great importance in regard to its action on the soil, but the assumption that the activity increases with the degree of fineness is erroneous. With an increase in the amount of lime contained in the soil, it is best to use finely-divided superphosphates, whilst in the case of soils poor in lime it is preferable to employ a coarser powder.

D. B.

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## Analytical Chemistry.

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**Nickel Alkali-proof Vessels.** By W. DITTMAR (*Chem. News*, 50, 3—6).—The production of nickel is referred to (comp. this vol., 129), and its use recommended for operations with caustic alkali-leys. In its resistance to the action of alkali-leys, it is equal to platinum, whilst for its cheapness, hardness, density, and lower conductivity of heat, it surpasses silver. The latter quality allows the operator to lay hold of a dish containing boiling caustic potash-ley with his bare fingers. Its density prevents the retention of potash, as is the case with silver, and its hardness gives it permanence of form. Solutions of caustic alkalis are, however, not absolutely without action on nickel, for the metal is attacked when the strength of the solutions reaches about 60 per cent. of potash (or soda). The porosity of silver may be diminished by alloying it, and a very durable and useful alloy for fusions with alkalis has the composition silver 91, gold 7, and nickel 2 per cent. The author then proceeds to show that the action of fused alkalis on metals is due to the formation of peroxides, which then constitute the destructive reagent; since experiments prove that silver, the above alloy, platinum, and nickel are not acted on in the absence of air, and fusions with alkalis may be conveniently and safely conducted in platinum vessels in an atmosphere of hydrogen or nitrogen, for which purpose an arrangement is described in the paper: the alkalis then fuse quite steadily, and do not boil up as they do when fused in air. All these metals are attacked by fused alkalis in the presence of air, silver least. Potash and baryta are more energetic than soda. Some experiments with carefully prepared lithium compounds show that the carbonate when ignited in a platinum vessel in the air attacks the metal, and is itself in greater part converted into peroxide. When heated in hydrogen or nitrogen, it does not attack the metal, but gradually loses carbonic anhydride, and with the former gas nearly pure lithium oxide ( $\text{Li}_2\text{O}$ ) remains as an almost infusible solid, which does not readily combine with water; with nitrogen, part only of the carbonic anhydride is driven off. A blowpipe flame was employed to finish the lithium experiments.

D. A. L.

**Dumas' Nitrogen Apparatus.** By M. ILINSKI (*Ber.*, **17**, 1347—1349).—The author describes a modification of Dumas' apparatus, for which he claims the following advantages:—1. Ease of construction with ordinary apparatus of a laboratory, and easy replacement of damaged parts. 2. Absence of all fragile glass parts, and of india-rubber tubing in contact with the caustic soda solution. 3. Working under a constant and very small pressure.

The apparatus needed consists of an ordinary burette, a large stoppered bottle, some glass tubing and a few corks; but the arrangement of the apparatus cannot be clearly explained without the drawing.  
L. T. T.

**Detection of Nitrogen in Organic Compounds.** By C. GRAEBE (*Ber.*, **17**, 1178).—The nitrogen in diazo-compounds cannot be detected by heating them with metallic potassium, as the nitrogen escapes before any cyanide is formed.  
W. C. W.

**Coloured Tubes for Nesslerising.** By A. A. BRENNEMAN (*Chem. News*, **49**, 281—282).—From numerous observations, the author concludes that to obtain a satisfactory standard of comparison for Nesslerising, the coloured medium, best of glass, must be placed at or near the bottom of the testing tube, which is otherwise made of colourless glass. When used, it must be filled up to the mark with clear water. Such tubes are made by fusing a short piece of amber-glass tubing to a longer piece of the ordinary colourless tubing used for Nessler tubes; and when the required tint has been secured by blowing the amber glass, the tube is closed and flattened at the bottom.  
D. A. L.

**Standard Soap Solution.** By L. GARNIER (*J. Pharm.* [5], **7**, 482—483).—As standard soap solution is liable to deposit a precipitate which is not redissolved by heat, it is necessary to restandardise the solution after filtering. For this purpose, the author uses a standard solution of calcium chloride containing 0.25 gram of  $\text{CaCl}_2$  in one litre of water or a solution of barium nitrate containing 0.5878 gram in one litre. The strength of the solution having been ascertained, the degrees of hardness of a water can be found by calculation in the ordinary way.  
W. R. D.

**Phenolphthaleïn as Indicator in the Estimation of Carbonic Anhydride in Mixtures of Gases.** By R. BLOCKMANN (*Ber.*, **17**, 1017—1019).—This method of estimating the carbonic anhydride in air or in mixtures of gases containing no other acids, depends on the property of free carbonic anhydride to decolorise a solution of phenolphthaleïn. The estimation of carbonic anhydride in air may be made in a 500 c.c flask by means of a dilute lime-water containing two or three drops of a solution of 1 part of phenolphthaleïn in 1000 parts alcohol (60 per cent.) The test can be made either by adding this solution slowly and agitating until decolorisation takes place, or by using a fixed quantity of the alkaline solution, and refilling the flask

with air and agitating as often as is necessary to decolorise the indicator. The second method has been found the better.

A. B.

**Separation of Iodine and Chlorine in the Dry Way.** By J. KRUTWIG (*Ber.*, 17, 341—343).—If an intimate mixture of potassium iodide with excess of potassium dichromate be rather strongly heated in a crucible, the whole of the iodine is given off, a corresponding amount of potassium chromate and chromic oxide being left in the crucible. The estimation may be made by weighing the crucible before and after heating, when the loss is iodine, or by treating the residue with water. In the latter case chromic oxide remains undissolved and may be filtered off and weighed. Sodium chloride is not attacked by potassium dichromate, so that this method may be used as a means of separating chlorine and iodine in a mixture.

L. T. T.

**Liquid Paraffin as a Reagent for the Presence of Water in Alcohol, Ether, and Chloroform; and its Employment in the Preparation of Hydrobromic and Hydriodic Acids and of the Alkyl Iodides.** By L. CRISMER (*Ber.*, 17, 649—652).—The “liquid paraffin” of the German Pharmacopœia, is an oily liquid consisting of a mixture of hydrocarbons of the methane series; it distils between 215° and 240° under 6 mm. pressure. It mixes in all proportions with *anhydrous* ether or chloroform, and is slightly soluble in *absolute* alcohol. The liquids so obtained are perfectly clear, provided the solvents are really anhydrous, but if water is present even in very minute quantity the liquids are turbid. Liquid paraffin dissolves phosphorus in small quantity; it is a good solvent for chlorine, bromine, iodine, the chlorides and bromides of phosphorus and the alkyl iodides, chlorides, and bromides.

As the halogens unite with ordinary phosphorus placed under liquid paraffin without danger of explosion, if the liquid is well cooled, the trihaloid-compounds of phosphorus can be conveniently prepared by aid of this substance, and further by slowly dropping the calculated amount of water into the solution of phosphorous tri-bromide or iodide so obtained, pure and anhydrous hydrobromic or hydriodic acid are readily formed. Finally, ethyl iodide can be readily prepared by the action of anhydrous alcohol on a solution of phosphorous triiodide in liquid paraffin.

A. J. G.

**Test for Hydrogen Peroxide.** By M. TRAUBE (*Ber.*, 17, 1062—1064).—The characteristic reaction for hydrogen peroxide as given by Schoenbein, with potassium iodide, starch solution, and ferrous sulphate, requires that the liquid to be tested should be neutral. The author finds that the presence of very minute quantities of hydrogen peroxide may be detected in acid solution if a very minute quantity of cupric sulphate be added to the iodised starch solution, and then ferrous sulphate. This reaction depends on the fact that cupric iodide may exist in very dilute solution without any separation of iodine or formation of cuprous iodide (this vol., p. 962). Iodine is only

separated on addition of ferrous sulphate in presence of hydrogen peroxide. A. B.

**Rapid Estimation of Nitrates.** By E. FALIÈRES (*Ann. Agronomiques*, **10**, 125—131).—The method proposed by the author is a combination of a modification of Pelouze's process with Bruel's recently described volumetric method of estimating ferric chloride.

0.500 gram of iron in impalpable powder (iron reduced by hydrogen or very finely powdered) is placed in a flask holding about 50 c.c. and treated with 10—12 grams pure fuming hydrochloric acid. The iron dissolves almost instantaneously, especially if the flask be *very slightly* warmed, and the solution is free from traces of ferric salt. 0.200 gram pure sodium nitrate dissolved in 10—12 c.c. water is added to the solution of ferrous chloride, and the mixture boiled until all nitrous vapours are expelled and the liquid has cleared. It is then immediately diluted to 200 c.c. with recently boiled distilled water. For the titration 10 c.c. of this liquid are taken (= 0.010 gram  $\text{NaNO}_3$ ), transferred to a flask of 150 c.c. capacity, diluted to 50 or 60 c.c. with boiled distilled water, and coloured deep violet by the addition of about 0.100 gram sodium salicylate. The liquid is now boiled, and sodium hyposulphite solution (4 grams per litre) is added gradually from a burette graduated to 0.1 c.c., the liquid being boiled between each addition of hyposulphite. The following reaction takes place:—



and the liquid is gradually decolorised. The end point is marked by the faintest rose-tint perceptible to the eye; and the process is sensitive to 1 drop of hyposulphite. When this point is reached, a second 10 c.c. of the  $\text{NaNO}_3$  is added to the decolorised liquid, and the titration repeated, the mean of the two results being taken. The value of the standard hyposulphite having thus been ascertained in terms of pure sodium nitrate, the determination of nitric nitrogen in crude nitrate of soda and potash, or mixed manures, is made in precisely the same manner as above described. Organic matter is without influence on the result. A mixture containing 10 per cent. nitrate of soda with arachida cake, sulphate of ammonia, potassium chloride, superphosphate, gypsum, and sand, gave perfectly correct results. Dried blood and guano substituted for arachida cake did not affect the correctness. J. M. H. M.

**Testing for Nitric Acid and Nitrates in Vegetable Tissues.** By A. ARNAUD and L. PADÉ (*Compt. rend.*, **98**, 1488—1490).—Cinchonamine nitrate (this vol., 87) is almost absolutely insoluble in dilute acids, and when an acid solution of a salt of cinchonamine, preferably the hydrochloride, is mixed with a solution containing even a very small quantity of nitric acid or a nitrate, cinchonamine nitrate forms in small distinct crystals, easily recognisable under a microscope. This reaction may therefore be used for the detection and possibly estimation of minute quantities of nitrates.

This method may be successfully applied to detect nitrates in the juices of plants and also in the tissues. A section of the stalk or

other organ is immersed in a dilute acid solution of cinchonamine hydrochloride (0.4 per cent.) for some time and then examined under the microscope, when crystals of cinchonamine nitrate are seen encrusting the tissues and enclosed in the cells, and their relative abundance shows the relative distribution of nitrates in the organ examined.

Cinchonamine is at present a rare product, but *Remigia purdiana*, from which it is prepared, grows abundantly in America.

C. H. B.

**Commercial Assay of Native Phosphates.** By DUGAST (*Ann. Agronomiques*, 10, 10—14).—The author points out that the results obtained by the "commercial" method, viz., treating the mineral with nitric or hydrochloric acid, adding ammonia, and weighing the ammonia precipitate, are liable to great variation not only with the different phosphates employed, but also with the same phosphate under different conditions of treatment. The ammonia precipitate filtered off immediately after precipitation gives results more than 1 per cent. lower than when allowed to stand three hours before filtration. Precipitation in a hot solution and the use of boiling water for washing give over 1 per cent. less than when these operations are conducted in the cold. The use of nitric acid in dissolving the mineral may be made to give higher or lower results than hydrochloric acid, according to the subsequent treatment.

Preliminary calcination of the mineral generally lowers the result. A determination made on 1 gram may be lower than one made on 5 grams by as much as 2 per cent. Besides the two oxides of iron, alumina, and lime, in combination with phosphoric acid, the precipitate carries down an excess of lime and some magnesia. The oxides of iron and alumina are not always wholly combined with phosphoric acid, hence the quantity of lime in the precipitate varies, and with it the total weight of the precipitate.

J. M. H. M.

**Reverted Phosphoric Acid.** By T. S. GLADDING (*Chem. News*, 50, 1—3).—The present communication contains an account of experiments on the application of ammonium citrate for the determination of reverted phosphoric acid in natural phosphates, artificial soils, and natural soils. Similar experiments with artificial mixtures have already been described (*Abstr.*, 1882, 1319—1320).

Of natural phosphates, 25 varieties were examined, and five experiments were tried with each; in each case a gram of finely-powdered phosphate and 50 c.c. of a neutral solution of ammonium citrate, sp. gr. 1.09, were corked up in a flask and digested for 30 minutes. Experiment (1), at 40°; (2), at 65°; (3), at 65°  $\frac{1}{2}$  c.c. 20 per cent. ammonia being added for each 50 c.c. of citrate; (4), at 65°, with 1 c.c. 20 per cent. ammonia; (5), at 65°, with 0.753 gram citric acid to every 50 c.c. of citrate solution. The results are tabulated, showing the percentage of phosphoric acid dissolved in each experiment, and the following conclusions are deduced with regard to the condition of the ammonium citrate solution. Slight acidity largely increases the solvent action on the crude phosphates; slight alkalinity, on the other hand, decreases the solvent action on all calcium phos-

phates, and this decrease is intensified with stronger alkalinity; the converse, however, is the case with iron and aluminium phosphates, for alkalinity increases the quantity dissolved by the ammonium citrate solution. From these conclusions, it is evident that neutral citrate solution is preferable to either acid or ammoniacal (comp. this vol., 639). The change of temperature from 40° to 65° is unimportant with natural phosphates. Artificial soils were prepared for the experiments, 5 grams of sand were mixed with 0.25 or 5 grams calcium carbonate, or 1 gram iron oxide, or 1 gram aluminium hydroxide, all freshly precipitated, or 30 grams of sand were mixed with 3 grams of brown hematite or bauxite; with the last two, a solution of 0.75 gram sodium ammonium phosphate was employed; in the other cases the quantity used was 0.5 gram, with the exception of the first, with which only 0.2 gram was taken. These mixtures were exposed in open vessels either in shade or in the sun for 72 hours; they were then divided into two equal parts and digested with ammonium citrate solution for 30 minutes, one portion at 40°, the other at 65°; with the hematite and bauxite, however, three equal parts were taken, one being treated with cold water, in addition to the above digestion. The results are thus summarised:—Ammonium citrate solution dissolves all the reverted calcium phosphate at 40°, whereas in the other experiments all the reverted iron and aluminium phosphates were dissolved at 65°, but not completely at 40°.

D. A. L.

**Estimation of Carbonic Anhydride in Air.** By M. BALLO (*Ber.*, 17, 1097—1101).—This method is based on the property of carbonic anhydride to decolorise a solution of phenolphthaleïn. The author, however, finds that lime-water absorbs carbonic anhydride from the air too slowly for practical purposes, and in place of it he uses a solution containing caustic potash and barium chloride. This solution when shaken with atmospheric air absorbs carbonic anhydride with much greater rapidity, and has also the advantage of preventing the formation of a bicarbonate, as the carbonic anhydride absorbed is at once precipitated as barium carbonate. The solution is made of such a strength that 1 c.c. = 1 c.c. CO<sub>2</sub> in 10,000 c.c. of air. The estimation is made in a flat-sided flask (this form being used for convenience in shaking) of about 500 c.c. capacity, in the following way:—The flask is filled with the air to be tested and closed with an india-rubber stopper. A quantity of the alkaline solution slightly coloured with phenolphthaleïn, sufficient for the observation of the normal quantity of carbonic anhydride in air, is run in and briskly shaken. If the quantity of carbonic anhydride is greater than the normal, decolorisation takes place in one or two minutes. A second quantity is then run in and again shaken, and the addition of these quantities of solution continued until the solution remains coloured after at least three minutes' shaking. The quantity of solution required may be more exactly measured in a second determination. In this way, in 10 or 15 minutes, the carbonic anhydride in air can be estimated with fair exactness, and the author's results differ but slightly from those obtained by Pettenkofer's method. For example, in a schoolroom, 42.6 vols. CO<sub>2</sub> per 10,000 of air were found using a flask of

580 c.c. capacity, and 37.6 vols.  $\text{CO}_2$  with a flask of 800 c.c. capacity, whilst by Pettenkofer's method 42.1 vols.  $\text{CO}_2$  were found. As a rule, however, the results of other examples given by the author are somewhat lower than those by Pettenkofer's method. By using a flat-sided flask, the labour of shaking is diminished, and the absorption is quicker in a flask of 500 c.c. than in a larger one. The solution of potash and barium chloride should not be coloured until the experiment is about to be made, as it has been observed that the coloured solution becomes decolorised after a time. A. B.

**Volumetric Estimation of Carbon Bisulphide in Thiocarbonates.** By E. FALIÈRES (*Ann. Chim. Phys.* [6], 2, 134—144).—The application of potassium thiocarbonate on a large scale for the destruction of the phylloxera necessitates the introduction of some simple method for their analysis, with especial regard to the coloration of the carbon bisulphide contained. Gélis has proposed to add sulphurous acid to a given volume of the solution; this precipitates the carbon bisulphide, the volume of which is measured. But this method is inexact, owing to the incomplete separation of the carbon bisulphide and the difficulty of exactly estimating the true volume. It is here proposed so to modify the process that exact results can be obtained; the method adopted is as follows:—The density of the solution is first taken, and then a volume of it corresponding to 10 grams by weight is measured off; this is mixed with its own volume of water placed in a partly closed measuring vessel, together with a few cubic centimetres of benzene, and a solution of sulphurous acid is then added gradually so as to precipitate the carbon bisulphide; this is dissolved by the benzene, the solution being facilitated by agitation. The increase in the volume of the benzene due to the carbon bisulphide is then noted, and the mass corresponding with this volume calculated and referred to the mass of the solution of sulphocarbonate originally taken. The method presents the advantages of simplicity, rapidity, and a sufficient degree of accuracy for practical purposes. In the original paper, tables are given of the values of thiocarbonate solution of different densities corresponding with a mass of 10 grams, and of the percentage of carbon bisulphide corresponding with a definite increase of volume of the benzene. V. H. V.

**Separation of Strontium from Calcium.** By I. BOGOMOLETZ (*Ber.*, 17, 1058—1061).—The separation of these metals by means of a solution containing 20 per cent. of ammonium sulphate and 3 per cent. of ammonium oxalate as given by Sidersky (*Abstr.*, 1883, 509), has been repeated and investigated. The method, in the author's opinion, is about the same, as far as simplicity goes, as Rose's ordinary method. The use of it depends on the conditions (quantity of substances, time, and temperature) which influence the reaction. A. B.

**Estimation of Alum in Wine.** By P. CARLES (*J. Pharm.* [5], 7, 373—376).—The author finds that the methods usually adopted for estimating the amount of alum in wine are defective, the phosphates of the alkaline earths being precipitated with the alumina. The following process is recommended:—Half a litre of wine is evaporated



to dryness and the residue carbonised by ignition. The carbonaceous mass is powdered and boiled with dilute hydrochloric acid, and excess of solution of soda is added to the filtered liquid while still hot; the phosphates are thus precipitated and the alumina dissolved. The filtered liquid is treated with ammonium chloride, and after it has been boiled for a few minutes the alumina is filtered off. To free the precipitate from potassium salt, which it obstinately retains even after prolonged washing, it is redissolved in hydrochloric acid and the solution precipitated by ammonia; after being washed, the precipitate is calcined and weighed. The results are sufficiently accurate for ordinary purposes, but a part of the alumina remains as phosphate, thus instead of 0.108 gram of alumina, 0.124 and 0.131 gram were obtained.

W. R. D.

**Estimation of Lead in Tinplate.** By P. CARLES (*J. Pharm.* [5], 7, 285—287).—It is often necessary to detect and estimate lead in the tinplate which is used in making cases for preserved fruit, foods, &c. When tin and lead are alone present, the two metals can be treated with nitric acid, when the tin remains as stannic acid, and the lead can be precipitated from the filtrate as sulphate. This process is not accurate when iron is present, as the greater part of the tin is converted into ferric stannate, which remains in the filtrate, and is precipitated with the lead sulphate when sulphuric acid is added. The author recommends dissolving the tinplate in hydrochloric acid with a little nitric acid, and after expelling all the nitric acid by ebullition, to dilute the liquid and precipitate with hydrogen sulphide. The mixed tin and lead sulphides are separated by digestion with ammonium hydrosulphide. The tin is subsequently converted into stannic acid, and the lead into sulphate.

W. R. D.

**Reaction to Detect the Presence of Metallic Iron.** By A. v. LASAULX (*Jahrb. f. Min.*, 1884, 2, Ref., 33).—The magnetic portion of the powdered substance is treated with a solution of tungstic acid, and placed under the microscope. The smallest particles of iron are surrounded with a blue edge. Organic matter, zinc, and copper must be absent.

B. H. B.

**Estimation of Iron and Stannous Salts by Potassium Chromate.** By L. CRISMER (*Ber.*, 17, 646—649).—A modification of Löwenthal and Stromeyer's method (*Annalen*, 171, 261), the final titration being effected by decinormal potassium chromate, with potassium iodide and starch as an indicator, instead of by potassium permanganate.

A. J. G.

**New Reaction for Pyrogallol.** By O. NASSE (*Ber.*, 17, 1166).—Iodine gives a transient purple coloration with aqueous or alcoholic solutions of tannin, gallic acid, and pyrogallol, in presence of minute quantities of neutral or acid salts. This reaction is not exhibited by phoroglucinol, querciglucinol, or ellagic acid. The presence of salts in water may be demonstrated by the formation of the purple coloration on the addition of a mixture of gallic acid and iodine.

W. C. W.

**Behaviour of some Fats and Lubricating Oils with Glacial Acetic Acid.** By E. VALENTA (*Dingl. polyt. J.*, 252, 296).—From

a series of experiments, the author infers that most animal and vegetable fats are more or less soluble in glacial acetic acid. Equal parts of oil and glacial acetic acid were intimately mixed in a test-tube and subjected to various temperatures. Olive oil and castor oil are completely soluble at the ordinary temperature (15—20°); palm oil, laurel oil, cocoanut oil, palm-nut oil, illipe oil, olive oil, cacao butter, sesame oil, peach-kernel oil, almond oil, cotton oil, earth-nut oil, apricot-kernel oil, beef tallow, American bone fat, cod-liver oil, and pressed tallow are completely, or almost completely soluble at temperatures varying between 23° and the boiling point of glacial acetic acid, whilst rape oil and mustard oil (cruciferous oils) are imperfectly soluble in boiling glacial acetic acid. The subjoined table gives the results of experiments made with a view to distinguish various fats by warming equal volumes of fat and glacial acetic acid in a test-tube

Name of fat.	Sp. gr. at 15°.	The solution in equal parts glacial acetic acid (sp. gr. = 1·0562) is rendered turbid at	Remarks.
<i>Vegetable fats.</i>			
Palm oil .....	—	23°	Fresh fat procured from the Brunn candle works.
Laurel oil .....	—	26—27°	Old rancid fat from a collection in the laboratory.
Cocoanut oil .....	—	40°	From the laboratory collection.
Illipe oil .....	0·9175	64·5°	Extracted from the seeds of <i>Bassia longifolia</i> .
Palm-nut oil .....	—	48°	Old rancid fat from the English market.
Green olive oil .....	0·9173	85°	Oil from second pressing, contains presumably large quantities of olive-kernel oil.
Cacao butter .....	—	105°	Obtained from J. Stettner.
Sesame oil .....	0·9213	107°	Ditto.
Peach-kernel oil .....	0·9241	108°	Crude oil. Hungarian source.
Almond oil .....	0·9186	110°	Obtained from J. Stettner from sweet almonds.
Cotton oil .....	0·9228	110°	Obtained from J. Stettner.
Olive oil (yellow) .....	0·9149	111°	Oil from first pressing, obtained from J. Stettner.
Earth-nut oil .....	0·9193	112°	Obtained from J. Stettner.
Apricot-kernel oil .....	0·9191	114°	Ditto.
<i>Animal fats.</i>			
Beef tallow .....	—	95°	Hard tallow from Italy.
American bone fat .....	—	90—95°	
Cod-liver oil .....	—	101°	Obtained from Vienna.
Pressed tallow .....	—	114°	Melting point 55·8°. Very hard and pure.

until a clear solution is obtained, allowing to cool, and observing the temperature at which the clear solution is rendered turbid.

In conclusion, the author mentions that, by the aid of glacial acetic acid at 50—60°, it is possible to detect adulterations of mineral oils with resin oils, the latter being readily soluble in acetic acid, whilst mineral oils are almost insoluble in that solvent. D. B.

**Assay of Quinine Sulphate.** By H. BYASSON (*J. Pharm.* [5], 7, 291—294).—The author proposes the two following methods for the assay of quinine sulphate:—

*Method I.*—This is a modification of the method of the French Codex. An ordinary test-tube of about 15 mm. diameter is graduated with one mark (*a*) to hold 6 c.c.; a second mark (*b*) is then made above this to indicate 2 c.c. from the first mark. 0.5 gram of the quinine sulphate is introduced into the tube, and then washed ether added to the mark (*a*); sufficient solution of ammonia (0.9—0.950) is finally added to exactly reach (*b*). The tube is then fitted with an air-tight cork and well shaken. If the quinine sulphate be pure, no trace of a flock or crystal will be visible between the layers after the liquids have separated. This method is capable of detecting from 3—4 per cent. of cinchonine sulphate, 4—5 per cent. of quinidine sulphate, and from 5—6 per cent. of cinchonidine sulphate.

*Method II.*—In this method, Laurent's polarimeter is used. 0.5 gram of quinine sulphate is placed in a flask graduated to 50 c.c., and dissolved by the addition of dilute sulphuric acid (2 per cent. by volume). In this way a 1 per cent. (by volume) solution of quinine sulphate in dilute sulphuric acid is obtained. The 22 cm. polarimeter tube is filled with the solution, and the rotatory power of the liquid determined. Commercial quinine sulphate should possess, at 15°, a rotatory power of not less than  $-22^\circ$  on the saccharimetrical scale. When the deviation is less than  $-21.8^\circ$ , the quinine sulphate should be chemically examined by the first method. The following are the rotatory powers in saccharimetrical degrees of 1 per cent. (by volume) solutions of the pure sulphates of the cinchona alkaloids. The observations were made in the 22 cm. tube of Laurent's polarimeter:—

Quinine sulphate.....	=	$- 23.3^\circ$
Cinchonidine sulphate....	=	$- 16.5^\circ$
Quinidine sulphate .....	=	$+ 26.4^\circ$
Cinchonine sulphate.....	=	$+ 22.2^\circ$

Commercial quinine sulphate usually shows a deviation of  $-22^\circ$ . A deviation of  $-21.8^\circ$  indicates the presence of about 5 per cent. of cinchonidine sulphate, and a deviation of  $-20^\circ$  about 10 per cent. of cinchonidine sulphate. W. R. D.

**Analysis of Flour.** By A. R. LEEDS (*Chem. News*, 49, 269—273; 280—281).—The present communication contains an exposition of the inconsistencies and fallacies of certain erroneous reports, published in America, wherein various samples of flour and farinaceous preparations are condemned, mostly on evidence obtained by microscopical examinations, from which are drawn quantitative analytical conclusions. The defects of these observations and inferences are

explained in detail, as also are those of a process for the determination of gluten, starch, &c., in flour, described in the same reports. In this process, the weighed quantity of flour is moistened, and the dough put into a piece of muslin and kneaded with a fixed quantity of water, the ultimate residue in the muslin being regarded as gluten. The latter part of the communication consists of comprehensive comments on the imperfections of the analytical process, Cairn's method, frequently employed for the complete examination of flour.

D. A. L.

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## Technical Chemistry.

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**Expedients for rendering Photographic Films sensitive to Green, Yellow, and Red Rays.** By H. W. VOGEL (*Ber.*, 17, 1196—1203).—Silver tetrabromofluorescein is not decomposed by dilute acetic acid. It is remarkably sensitive to greenish-yellow rays. If a cadmium bromide collodion plate containing eosin is immersed in a silver solution, its sensitiveness to blue rays is very much diminished and the action of the yellow rays is greatly increased. The addition of eosin to collodion silver bromide containing a small quantity of silver iodide produces a film which is sensitive to yellow and to blue rays.

In photographing coloured objects, a yellow glass is introduced between the object and the apparatus in order to diminish the action of the blue rays. With such an arrangement, Schweinfurt green and yellow appear light. The action of orange and red rays may be increased by adding methyl-violet or aldehyde-green respectively to the silver bromide collodion.

Wet gelatine plates containing eosin are much more sensitive to yellow rays than the dry plates. W. C. W.

**Transmission of Cholera by Drinking Water.** (*Dingl. polyt. J.*, 252, 261.)—Koch has succeeded in detecting certain bacilli in the intestines of persons who have died of cholera in Egypt and Calcutta. He isolated and cultivated these bacilli, and on subjecting them to minute examination, made a number of characteristic observations in regard to their form and their development in nutritive gelatin, by means of which they can be distinguished with certainty from other bacilli. With this, it was possible to definitely decide the question, whether these bacilli are contained in the intestines of all bodies, or whether they occur only in the intestines of cholera patients. By the aid of gelatin cultivations, the presence of these organisms in the evacuations of cholera patients, as well as in the intestines of cholera corpses, was clearly demonstrated, whilst on investigating the intestines of other corpses, cholera bacilla could not be detected.

It has been shown that since 1870 a considerable reduction has taken place in the spread of cholera in Calcutta. Before 1870, the cholera carried off annually 10·1 persons out of every thousand, whilst

since 1870 the death-rate has fallen to three persons per 1000. It is thought that this circumstance should receive due consideration, as it points to the means of effectually keeping off this disease. It is the unanimous opinion of the medical profession that this decrease has been effected in consequence of the introduction of waterworks in Calcutta. Koch has shown that the cholera often settles in a particular locality, and displays its greatest virulence in certain quarters. Such epidemics are frequently observed in the surroundings of the so-called "tanks," which are small ponds or wells enclosed within huts. The neighbours obtain their water supply from these tanks, and simultaneously utilise them for various purposes, such as bathing, washing clothing, cleaning domestic utensils, &c. It is worthy of note that in order to prevent the destruction of cholera bacilli, it is necessary to preserve them in a moist place. In liquids, their development is maintained for a long time, a circumstance which indicates that these germs are carried from place to place, and transmitted from person to person in a moist state only.

D. B.

**Hydrogen Peroxide in Medicine.** By E. SONNERAT (*J. Pharm.* [5], 7, 488—496).—The author finds that solutions of hydrogen peroxide are most stable when dilute and slightly acid with sulphuric acid, and hence recommends the use of such solutions in medicine. Thus a 1-volume solution, which was slightly acid with sulphuric acid, did not alter in strength for one month when kept in a stoppered bottle. The hydrogen peroxide of commerce is very acid in reaction, and often contains 15 grams of sulphuric acid per litre; some samples contain hydrochloric acid and barium chloride. The sulphuric acid in commercial specimens may be estimated and removed by means of a standard solution of baryta-water. The author estimates the oxygen value of these solutions by first making them alkaline with soda, and then adding manganese dioxide. The operation is conducted in an Esbach's ureometer tube, and the volume of free oxygen measured in the usual way. Full details of the method are given in the original paper.

W. R. D.

**Manufacture of Sulphuric Acid from Pyrites in America.** By G. LUNGE (*Dingl. polyt. J.*, 252, 293—295).—Referring to a previous communication (*ibid.*, 248, 35), the author mentions that although American pyrites mostly contains arsenic, the Sulphur Mines Company of Virginia and the mines of the Davis Company and others yield a pyrites which is perfectly free from arsenic, so that the manufacture of pyrites acid, as compared with sulphur acid, must be more remunerative in America than in Europe. According to Voelcker, pyrites from the Sulphur Mines Company has the following composition:—

S.	Fe.	Fe <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> .	SiO <sub>2</sub> .	Cu.	As.
48·02	42·01	1·93	0·44	7·60	—	—

The author is of opinion that with the large quantities of pyrites found in America, and the fact that a number of companies have been formed with the object of working the pyrites mines, the price of pyrites acid will have to suffer considerable reduction.

D. B.

**Separation of Arsenic from Saline Solutions.** (*Dingl. polyt. J.*, 252, 304.)—According to Glaser, of Berlin (Ger. Pat., 26,632, March, 1883), saline solutions contaminated with arsenic or arsenious acid are concentrated, neutralised, and treated with stannic acid, antimonious or antimonious acid or peroxide of lead, until the filtrate is free from arsenic. The precipitate is separated from the saline solution, washed with water, and treated with dilute sulphuric or nitric acid, the arsenic being dissolved, whilst the residue, after washing with water, may be used for the purification of fresh quantities of saline solutions. D. B.

**Novelties in the Iron Industry.** (*Dingl. polyt. J.*, 252, 243—253.)—It is generally assumed that the Bessemer process can be worked with advantage only by operating on large quantities of iron. Tunner, however, draws attention to three modes of conducting this process on a small scale. The most important process is that which has been worked since 1877, with great success, at Avesta in Sweden. The works belonging to the Jern-Contor Company contain two blast furnaces, two Bessemer converters (with two spare converters), and a rolling mill for the production of plates. The total working power amounting to from 800 to 900 e., is obtained from the River Dalelfoen. The process is described in detail in the original paper. Contrary to the generally accepted opinion that the success of the Bessemer process depends on its magnitude, Ehrenwerth infers that the process in work at Avesta proves, (1) that it is possible to obtain the temperature necessary to complete the Bessemer process with small charges and to produce a very soft metal from pig-iron, containing only a small amount of manganese and less silicon than is contained in the iron worked in the alpine districts (charcoal-Bessemer process); (2) the consumption of ferromanganese and the amount of manganese contained in the metal is less than is the case in the production of similar qualities of iron by the processes employed in Styria; (3) the Bessemer process may be applied to the continuous production of soft, fibrous iron, and is the best process for obtaining a uniform product.

The second process referred to by Tunner originates with a French firm, and is worked in France, and by Vogel and Nuth in Austria in the Murz Valley. Converters resembling the stationary ovens formerly worked in Sweden are used. The third process is the so-called pneumatic process of making wrought iron introduced by Chapin of Chicago, which consists in combining the Bessemer process with a puddling process conducted in rotary furnaces. The advantage of this process is the production of iron in the form of balls.

In order to regulate the temperature in acid converters during the blowing, Jones (Am. Pat., 287,687, Oct., 1883) recommends the introduction of steam into the metallic bath.

According to the Société John Cockerill of Seraing (Ger. Pat., 24,971, April, 1883), it is proposed to utilise the heating furnaces of steel works for the "soaking" of steel ingots.

Cooper of Linthorpe (Ger. Pat., 25,486, Dec., 1882) effects the

soaking of steel castings in an underground tunnel extending from the casting pit to the rolling mill.

Gjer's so-called "soaking pits" are used at the works of the Scranton Steel Co. From 80 to 85 per cent. of the steel ingots produced are brought to a uniform temperature in these pits, after which they are rolled into rails without further heating. D. B.

**Novelties in Metallurgy.** (*Dingl. polyt. J.*, 252, 211—217.)—For the examination of commercially pure copper, Pufahl tried the galvanic deposition in a platinum dish of about 30 grams copper by two small Grove's elements. The copper was contained as sulphate in 600 c.c. of solution to which 40 c.c. nitric acid of 1.2 sp. gr. had been added. After twelve hours only 0.5 gram copper remained in the solution, which was removed by the introduction of a current from four large Meidinger's elements without carrying down arsenic or antimony. For the estimation of oxygen in copper, 10—20 grams of bright copper turnings not exceeding 1 mm. in thickness were weighed into a porcelain boat placed in a glass or porcelain tube and heated to 500° in a current of pure hydrogen gas, the turnings having been previously treated with ether in order to remove all fatty particles. The loss in weight was calculated as oxygen. If the copper contains much arsenic, the percentage of oxygen should be determined from the weight of water collected in a calcium chloride tube. Analyses of the following brands are given:—

	Wallaroo.	C.H.M.Co.	Mansfield R.	Bede.	Grange.
Copper ....	99.795	99.864	99.491	99.148	98.961
Oxygen ...	0.127	0.120	0.145	0.090	0.160
Lead .....	0.004	—	0.038	0.023	0.005
Iron .....	0.001	traces	0.001	0.001	0.004
Nickel .....	0.039	0.002	0.201	0.081	0.066
Silver ....	0.015	0.028	0.031	0.058	0.010
Gold .....	—	traces	—	traces	—
Sulphur ..	—	—	—	0.005	traces
Arsenic....	—	traces	0.072	0.600	0.766
Antimony..	—	—	traces	0.002	0.011
	99.981	100.014	99.979	100.008	99.983

According to Egleston, the extraction of gold and silver from ores by means of sodium thiosulphate has been adopted by the Old Telegraph and Lexington Mills, the works at Triumfo and of the Geddes and Bertrand Mine at Eureka in Nevada, where an impure ore of the following composition is worked up.

SiO <sub>2</sub> .	Fe.	Zn.	Pb.	As.	Sb.	Ag.	CaO.
50.25	8.06	7.62	4.64	0.73	1.35	0.17	4.92
	MgO.	S.	CO <sub>2</sub> .	Cu.	Bi.		
	2.40	0.96	8.30	traces.			

The ore is crushed between rollers, dried in cylinders and passed



through a pipe lined with magnets whereby particles of iron are removed. It is then disintegrated thoroughly, mixed with 3 per cent. of salt and roasted. At the Bertrand works, the roasting is effected in four Brückner's rotary cylinders (*ibid.*, 219, 57), which are 2.1 m. wide, 5.8 m. long, and hold a charge of 5 tons. The roasting is completed in from eight to eleven hours, after which the ore is dropped into pits where it remains for nine hours. It is then transferred to the lixiviating apparatus, which consists of a series of vats 1.82 m. in diameter, and 0.91 m. deep, the bottom being covered with crossed wooden gratings and jute cloth between so as to form a filter. The ore is washed repeatedly with hot or cold water, and is then treated in the cold with a solution of sodium thiosulphate containing from 13 to 75 grams of salt per litre. If the ore contains gold it is preferable to use calcium thiosulphate, which is prepared by boiling lime with sulphur ( $3\text{CaO} + 12\text{S} = 2\text{CaS}_5 + \text{CaS}_2\text{O}_3$ ), allowing the mixture to settle, and passing in sulphurous anhydride until the clear solution ceases to give a precipitate with a dilute solution of silver chloride. The action of sodium thiosulphate on silver chloride is explained by the following equation:  $-2\text{AgCl} + 2\text{Na}_2\text{S}_2\text{O}_3 = 2\text{NaCl} + 2\text{NaAgS}_2\text{O}_3$ , the latter is extremely soluble in water. If the ore contains from 30 to 50 ounces of silver (0.093 to 0.155 per cent.), the amount of silver in the residue should not exceed 4 ounces (0.0124 per cent.). The argentiferous solution of sodium thiosulphate is then transferred to precipitating tanks and treated with a solution of calcium sulphide, when the following change takes place:  $-2\text{NaAgS}_2\text{O}_3 + 2\text{NaCl} + \text{CaS} = \text{Ag}_2\text{S} + 2\text{Na}_2\text{S}_2\text{O}_3 + \text{CaCl}_2$ . The silver sulphide is collected on a series of linen filters, washed with water and dried. It is then roasted in reverberatory furnaces or heated in retorts for the recovery of the sulphur.

Aaron proposes to agitate the precipitate of silver sulphide with lime and boil the mixture, calcium polysulphide being formed, which may be used for precipitating fresh quantities of silver chloride, whilst the residual grey mass consists mainly of metallic silver.

According to Groddeck and Brookmann, basic slag often exhibits a crystalline appearance. Some specimens contain thin, brown, rectangular, transparent plates having a hardness of 3.5°, and belonging to the rhombic system, whilst in others blue crystals are found. Analysis gave numbers agreeing with the formula for tetrabasic calcium phosphate:—

	CaO.	MgO.	MnO,	FeO.	P <sub>2</sub> O <sub>5</sub> .
Brown crystals.	58.01	0.88	—	2.93	38.75
Blue crystals .	56.00	—	3.00	6.00	35.00

D. B.

**Purification of Methylated Spirit.** By P. CAZENEUVE and CHAPUIS (*J. Pharm.* [5], 7, 126—130).—The authors have made experiments to discover to what extent the French methylated spirit, which is prepared by mixing wood spirit, containing about 25 per cent. of acetone, with ethyl alcohol, can be freed from its objectionable odour. By the action of nascent hydrogen from a zinc and copper couple placed in the spirit at a temperature of about 70°,

the disagreeable odour is completely removed after the reaction has gone on for five or six days. The same result can be obtained by using a zinc and copper couple in the cold, but the process takes about four times as long. By distilling the mixture from a water-bath nearly odourless spirit is obtained. The result is obviously due to the conversion of the acetone into secondary propyl alcohol by the action of the nascent hydrogen. Methylated spirit purified in this way could no doubt be used in the preparation of liqueurs and other substances intended for human consumption, and hence the authors consider that some substance other than impure wood spirit must be found for admixing with ethyl alcohol.

W. R. D.

**Analyses of the Wines of Médéah.** By BALLAUD (*J. Pharm.* [5], 7, 485—487).—The wines of Médéah (Algeria) possess all the characters of good red wines. The sp. gr. varies from 0·985—0·995, the alcoholic strength from 11—13 per cent., the total acidity calculated as sulphuric acid is from 3—4 grams per litre. These wines yield more extract (27—33 per cent.) than French wines, and an ash which contains much silica (0·84 per cent.) and potassium salts. The other constituents determined were glucose (2—3 per cent.), cream of tartar (1—2·6 per cent.), glycerol (6 per cent.).

W. R. D.

**Wines from Sugar.** By P. CARLES (*J. Pharm.* [5], 7, 14—24).—These wines (*vins de sucre*) are produced by refermenting the grape marc with a solution of sugar. The process consists in pouring off the natural wine from the marc and adding to the latter a lukewarm solution of sugar, this mixture is then allowed to undergo natural fermentation. The resulting wine is known as secondary wine (*vin second*), wine of the second press (*goutte*), wine of the second vat (*cuvée*), wine of the marc or sugar-wine (*vin de sucre*); the last name is that most commonly used in the south-west of France. In some cases crude solution of cane-sugar or raw crystallised sugar is employed in the process, in others starch-sugar in one or other of its different forms. The author has examined a great number of samples of these secondary wines and also of the natural wines, the results of the analyses being tabulated in the original paper. The wines analysed were of the 1880 vintage, and were produced in the provinces of Gironde, Dordogne, and Lot. The important inferences from the analytical results may be thus summarised: Crystallised sugar is to be preferred in the process, both for chemical and hygienic reasons, to starch-sugar; secondary wines are normally weaker in alcohol than natural wines, and contain less extractive matter, glycerol, hydrogen potassium tartrate, and substances which reduce cupric oxide (principally dextrose), as well as less inorganic matter; they are especially deficient in tannin and colouring matter. Secondary wines also greatly lack those volatile constituents which give bouquet (*vinosité*) to natural wines.

W. R. D.

**Kephir.** By H. STRUVE (*Ber.*, 17, 314—316).—The author gives a short historical sketch of the literature of *kephir*, showing that although this beverage has long been used in the Caucasus, and

was the subject of a scientific paper just a century ago, it is only since Kern's work on the subject (Abstr., 1883, 229) that attention has been given to it by the scientific world. The author is now investigating the whole subject of kephir-fermentation. L. T. T.

**Germinated Wheat.** By BALLAUD (*J. Pharm.* [3], 7, 295—301).—Owing to persistent rain in the north of France during harvest time, a quantity of wheat appeared in the market which had been much wetted, and in consequence had partially germinated. The author made a chemical examination of this wheat to see how far it differed from ordinary wheat. The constituents determined were moisture, acidity, lignin, gluten, fat, glucose, fixed salts, and substances soluble in cold water and in dilute acetic acid. It is seen from the tables of results which are given in the original paper that although there is no loss or variation in the quantity of total nitrogenous matter, yet the gluten has been profoundly affected, having become black, viscous, disintegrated, and partially converted into soluble albuminoids. An increase is observable in the quantity of glucose and lignin as well as of acid, and a decrease in the quantity of fat. The methods employed for estimating the constituents are fully described in the original paper. W. R. D.

**Secret Anti-incrustators.** By H. BELLMER (*Dingl. polyt. J.*, 251, 537—540).—"Lapidolyd" manufactured by Kolker Brothers in Breslau contained in 1 litre:—

	Specimen I. grams.	Specimen II. grams.	Specimen III. grams.	Specimen IV. grams.
Total residue . . . . .	85·67	68·23	92·73	64·42
Sodium carbonate ..	37·77	9·64	34·48	11·58
Sodium hydroxide ..	10·60	9·60	11·66	13·60
Sodium hydroxide combined . . . . .	0·85	8·75	—	—
Organic matter (cate- chu) . . . . .	28·84	31·10	35·98	31·44

Besides these substances, sodium chloride and the impurities usually present in caustic soda were found. One litre of lapidolyd is sold at 20 pfennigs, value about 4 pf.

"German incrustation solution" prepared by Patrosio in Bochum (I and II), and lapidolyd made by Neuerburg in Cologne (III) contained in one litre:—

	Na <sub>2</sub> CO <sub>3</sub> .	NaHO.	NaCl.	Na <sub>2</sub> SO <sub>4</sub> .	Organic.	grams.
I.	71·164	6·080	28·952	7·850	72·084	= 185·860
II.	84·300	15·200	8·120	5·000	27·168	= 139·788
III.	11·572	13·600	7·796	—	31·440	= 64·415

Albert in Berlin prepares an incrustation powder resembling "Paralithicon minerale" in chemical composition:—

	CaCO <sub>3</sub> .	NaCl.	CaH <sub>2</sub> O <sub>2</sub> .	NaHO.	Na <sub>2</sub> SO <sub>4</sub> .	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.	Glue.
	26·14	21·04	24·13	8·17	8·28	1·22	0·74	3·34	6·94

Marckmann's solution contains in 1 litre—

BaCO <sub>3</sub> .	CaCO <sub>3</sub> .	Sand.	Organic.	Na <sub>2</sub> CO <sub>3</sub> .	NH <sub>4</sub> Cl.	NaCl.	grams.
16·2	6·6	0·6	20·1	41·3	6·7	24·6	= 116·1

The powder introduced by Schwieger in Dessau, of which 100 kilos. cost 40s., consists of—

Na <sub>2</sub> CO <sub>3</sub> .	Na <sub>2</sub> SiO <sub>3</sub> .	NaCl and Na <sub>2</sub> SO <sub>4</sub> .	Organic.	Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .	Sand.	H <sub>2</sub> O.
14·36	12·50	0·92	14·60	0·75	12·49	44·23

“Desincrutant Ragosine” consists essentially of petroleum residues, and is used as a substitute for tar for painting the sides of boilers.

The anti-incrustating composition manufactured by Petrik and Co. in Bodenbach is a concentrated solution of impure sodium carbonate coloured blue with archil and treated with organic substances containing tannic acid. It also contains caustic soda and ammonia in small quantities. Its cost is 40 Austrian florins per 100 kilos.

“Disincrutant Marseillais” is brought into commerce from Manchester at 220s. per 100 kilos., and consists of an extract of tannin and catechu.

An extract of chestnuts is brought into commerce from Esseg in Hungary as a preventative of boiler incrustations.

The powder prepared by Zöpfke and Rudel in Berlin (100 kilos. at 96s.) has the following composition:—

Na <sub>2</sub> SO <sub>4</sub> .	NaCl.	Na <sub>2</sub> O.	CaO.	CO <sub>2</sub> .	H <sub>2</sub> O.	Glue.
15·46	14·88	12·62	28·32	8·51	14·32	5·89

The composition made by Hein in Halle is a vegetable extract containing tannin.

Hauff's solution contains mainly impure soda-ley coloured reddish-brown.

Engel recommends anti-incrustating solutions containing soda mixed with catechu; his “salt mixture” is composed of soda treated with salt.

The fluid known as Renz's “Soda caustique,” is impure caustic soda.

Ulmann of Zürich sells 100 kilos. of ordinary sea-weed (*Fucus vesiculosus*) at 150s. under the name of “Vegetaline.”

Kohn and Co.'s “Corrosiv” is mainly a mixture of soda and lime, and has the following composition:—

Na <sub>2</sub> O.	CaO.	NaCl.	CaCO <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .	Insoluble in HCl.	H <sub>2</sub> O.	Loss by ignition.
16·53	3·33	4·71	38·84	1·95	2·71	17·89	14·04

Harris Hewitt's “patent block composition” is a mixture of catechu and tannin wastes. D. B.

## General and Physical Chemistry.

**Electrochemical Equivalents of Silver and Copper.** By F. and W. KOHLRAUSCH (*Dingl. polyt. J.*, **253**, 32).—Comprehensive experiments show that a current of one ampère deposits per second 1.1183 mgrm. of silver, 0.3281 mgrm. of copper, or decomposes 0.09328 mgrm. of water. J. T.

**Change in Volume on Melting.** By R. SCHIFF (*Gazzetta*, **14**, 181—199, and *Annalen*, **223**, 247—268).—By means of a specially constructed dilatometer, the author has determined the specific gravities of several organic compounds at temperatures near their melting points. The following table shows the sp. gr. at the melting point, and the molecular volume of these bodies:—

	M.p.	Sp. gr.	Molecular volume at the melting point.
Dinitrobenzene .....	89.1°	1.369	167.66
Thymol .....	49.3	0.9499	157.55
Alphatoluic acid .....	76.4	1.0847	125.08
Nitrotoluene .....	54	1.1231	121.72
Anethol .....	21.3	0.9887	149.34
Dibenzyl .....	52.3	1.0423	174.21
Naphthalene .....	80	0.9777	130.61
Diphenyl .....	70.5	0.9961	154.25
Stilbene .....	119.2	0.9707	184.99
Phenanthrene .....	100.5	1.063	167.05
Ditolyl .....	120.8	0.9172	197.97
Acenaphthane .....	103	1.03	149.16
Dibromobenzene .....	89.2	1.8408	127.83
Dichlorobenzene .....	55	1.2499	117.37
Nitrophenol (ortho) .....	45.2	1.2945	107.64
(para) .....	114	1.2809	108.28
Benzoic acid .....	121.4	1.08	112.69
Stearic acid .....	69.5	0.8521	332.56
Dinitrotoluene .....	70.5	1.3208	137.51
Resorcinol .....	110	1.1795	93.94
Nitronaphthalene .....	61.5	1.2226	141.19
Benzene .....	4.4	0.8945	86.99
Phenol (Liebmann) .....	41	1.0606	88.42
Nitrobenzene (Kopp) .....	3	1.2029	102.03
Dibromobenzene (Körner) .....	-1	2.0	117.63

A close examination of these results shows that a constant alteration in composition does not produce a constant change of molecular volume at the melting point. This conclusion is directly opposed to that which Krafft (*Abstr.*, 1882, 1272, *Ber.*; **15**, 1171) arrived at from his research on the higher paraffins.

W. C. W.

**Solubility of Solid Substances in Water at various Temperatures.** By J. L. ANDRÉE (*J. pr. Chem.* [2] **29**, 456—477).—The author has repeated the estimations of the solubility of sodium chloride, potassium chloride, potassium nitrate, and potassium sulphate, as there are differences in the values obtained by various authors. He details the errors which may be made in the estimations, and describes, with the aid of drawings, the apparatus he has had constructed and has used. Three methods were employed in order to obtain saturated solutions:—1st. By using an excess of the salt and agitating with water at a constant temperature: regular and constant agitation was obtained by means of a hot air motor, and continued for  $1\frac{1}{2}$  hours, the salt falling through the water twice in a second. 2nd. By making a supersaturated solution, and agitating as before for  $1\frac{1}{2}$  hours. 3rd. By observing the temperature at which a known weight of salt dissolved in a known quantity of water. The first two methods were employed in a large number of estimations at different temperatures, and the third was employed to determine whether an excess of salt had any influence on the solubility: it was found to have none.

From the results obtained the author has obtained the following formulæ:—

NaCl (from 4° to 80°)

$$S = 35.63 + 0.007889(t - 4) + 0.0003113(t - 4)^2.$$

The solubility from 0—4° is constant.

KCl (from 4° to 60°)

$$S = 29.33 + 0.3206(t - 4) - 0.000577(t - 4)^2.$$

K<sub>2</sub>SO<sub>4</sub> (from 10° to 70°)

$$S = 9.219 + 0.19404(t - 10) - 0.0003083(t - 10)^2.$$

KNO<sub>3</sub> (from 4° to 60°)

$$\log S = 1.20412 + 0.019877(t - 4) - 0.0000882(t - 4)^2,$$

by the first method.

KNO<sub>3</sub> (from 4° to 60°)

$$\log S = 1.20385 + 0.019896(t - 4) - 0.0000883(t - 4)^2,$$

by the second method.

The difference in the two formulæ only affects the numbers in the second decimal.

A. B.

**Influence of Dilution on the Rate of Chemical Reactions.** By W. DE LA CROIX (*J. pr. Chem.* [2], **28**, 478—489).

**Combustion of Diamonds.** By C. FRIEDEL (*Bull. Soc. Chim.*, **41**, 100—104).—The author has submitted to combustion some particularly pure specimens of diamond. These diamonds were nearly colourless, and when ignited yielded very little ash. The combustion was conducted in a porcelain tube in a current of oxygen; this was prepared by heating a mixture of potassium chlorate and copper oxide, and was purified by passing it over heated copper oxide and through tubes containing potash, sulphuric acid, and phosphoric

anhydride. The combustion tube was connected with tubes containing sulphuric acid, phosphoric anhydride, and potash to collect the products of combustion, and was heated by a Wiesnegg grating, the diamonds being contained in a platinum boat. Full details of the construction of the apparatus, and the precautions which were observed are given in the original paper. Blank experiments were first made with the apparatus, which showed that there were no errors of importance. In the first experiment, 0.4705 gram of white Cape diamonds in small crystals was submitted to combustion. This quantity yielded 0.0007 gram of ash, which was deducted from the original weight of the diamonds. Calculating from the quantity of carbonic anhydride obtained, the atomic weight of carbon is 12.017 ( $O = 16$ ). Assuming the diamond to be pure carbon, and taking 12 as the atomic weight of carbon, the result represents a loss of 0.0021 gram of  $CO_2$ . In the second experiment, 0.8621 gram of perfectly colourless Cape diamond in 25 or 30 fragmentary crystals was burnt; this yielded 0.0005 gram of white flaky ash. With this correction, 12.007 is obtained as the atomic weight of carbon ( $O = 16$ ). The quantity of  $CO_2$  obtained represents a loss of 0.0015 on the theoretical amount ( $C = 12$ ).

In preliminary experiments, the combustion tube was of Bohemian glass, which was found to be unfitted for the purpose on account of its fusibility at the necessary temperature. In these experiments it was noticed that the partially burnt diamond was not, as is usually stated, transformed into coke, but presented a roughened and somewhat furrowed surface, much resembling in appearance a substance which had been immersed for a short time in an acid capable of attacking it. The ash obtained consisted of small white flakes, yellow in places and containing little black specks. Some of these flakes were attracted by the magnet, many were transparent, and among these were some which acted on polarised light, and therefore had retained their crystalline structure. Some of the Brazilian diamonds which were examined contained near the surface dark specks, which turned brown when heated without access of air to about the temperature of boiling cadmium. These diamonds, therefore, had probably been formed at a temperature lower than this. Dark specks were observed in other specimens which after exposure by fracture entirely disappeared before the blowpipe flame, and were probably carbonaceous.

W. R. D.

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## Inorganic Chemistry.

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**Preparation of Hydrobromic Acid.** By A. SOMMER (*Dingl. polyt. J.*, **253**, 215, from *Jour. Soc. Chem. Industry*, 1884, 20—23).—Hydrobromic acid may be prepared by four methods:—(1) Direct combination of bromine and hydrogen; (2) Decomposition of hydrogen-compounds, such as  $\text{H}_2\text{S}$ ,  $\text{HI}$ ,  $\text{NH}_3$ , and oils, by



bromine; (3) Decomposition of bromine compounds with fixed metalloids (especially  $\text{PBr}_3$ ); (4) Decomposition of metallic bromides by means of acids. Of the methods (1) to (3), only that with phosphorus pentabromide yields good results. The author proposes to decompose zinc bromide by sulphuric acid. The zinc bromide is easily prepared by acting on metallic zinc with bromine-water containing undissolved bromine. The solution is rapidly evaporated. To obtain the concentrated solution of hydrobromic acid ( $\text{HBr} \cdot 5\text{H}_2\text{O}$ , boiling at  $123^\circ$ ), 225 parts of zinc bromide are distilled with 180 parts of water and 196 parts of sulphuric acid, reckoned as monohydrate. To free the product from sulphuric acid, barium carbonate is added and the solution again distilled.

Sulphides are easily converted into sulphates by first warming them with nitric acid and then slowly adding concentrated hydrobromic acid. J. T.

**Supposed Recombination of Oxyhydrogen Mixture in the Dark.** By L. RICCIARDI (*Gazzetta*, 14, 20—23).—Rosetti, Zino, and Silvestri, in opposition to the universally received opinion, have stated that the gases composing oxyhydrogen mixture recombine slowly in the dark, if water is present. The author has carefully repeated Silvestri's experiments, and finds that no recombination takes place, even after the lapse of a year. C. E. G.

**Oxidation of Carbonic Oxide by Air and Moist Phosphorus.** By E. BAUMANN (*Ber.*, 17, 283—286).—In reply to the communication of Remsen and Keiser (this vol., 149), the author upholds the correctness of his former statements (*Abstr.*, 1882, 691, and this vol., 14), that carbonic oxide is oxidised to carbonic anhydride by air in the presence of moist phosphorus. He describes careful and elaborate blank experiments in which a stream of air was passed over moist phosphorus; but although the current was in some cases maintained for 96 hours, no trace of carbonic acid was obtained. Immediately pure carbonic oxide was mixed with the air, formation of carbonic anhydride took place. The author adds that *every* experiment was preceded by such a blank experiment, no disconnection or rearrangement of the apparatus being made between the two. L. T. T.

**Crystalline Form of Beryllium.** By W. C. BRÜGGER and G. FLINK (*Ber.*, 17, 849—850).—System hexagonal and holohedral  $a : c = 1 : 1.5801$ . Observed forms,  $\infty\text{P}$ ,  $\infty\text{P}2$ ,  $0\text{P}$ ,  $\text{P}$ , and sometimes  $\frac{1}{2}\text{P}$ . The habitus is either prismatic or tabular. These forms were observed on preparations made by Nilson and Pettersson, and also by Humpidge. Zinc also crystallises in holohedral hexagonal forms. H. B.

**Bismuth Subnitrate.** By M. GROSSMAN (*Arch. Pharm.* [3], 22, 297—307).—The only satisfactory method of testing bismuth subnitrate for arsenic is to heat it so as to drive off the nitric acid, and then treat it with zinc and hydrochloric acid; the evolved gases are tested with acidified silver nitrate solution (E. Reichardt, *Abstr.*,

1881, 195). Crude bismuth was converted into the sulphide by fusion with sulphur, and digested with caustic potash solution; the insoluble sulphide yielded a pure subnitrate. The method is, however, not suitable for manufacturing purposes, owing to the fusion of the separated sulphur during the action of nitric acid on the sulphide. The Hager-Deschamps process is the best: crude bismuth is dissolved in nitric acid, the solution poured into dilute ammonia, and the precipitated bismuth hydroxide washed with boiling water; zinc and lead present can be removed by boiling with caustic soda solution; the bismuth subnitrate obtained from the hydroxide is perfectly pure. The method of the German Pharmacopœia, 2nd edition—fusion with nitre and extraction with caustic soda—gives good results; whilst the method described in the 1st edition is uncertain. A modification by C. Schneider (Abstr., 1882, 18) yields better results, but is not sufficiently simple. H. B.

**Titanium.** By O. F. v. D. PFORDTEN (*Ber.*, 17, 727—730).—By heating titanium sulphide,  $TiS_2$ , in a stream of dry hydrogen free from every trace of oxygen, *titanium monosulphide* is obtained as a black substance insoluble in alkalis, soluble only with great difficulty in nitric acid and aqua regia, oxidised by fusion with soda and potassium nitrate.

Attempts to prepare a corresponding monoxide by reducing titanic oxide in a stream of hydrogen were unsuccessful, the reduction not proceeding beyond the deep indigo-blue oxide,  $Ti_3O_5$ . This oxide has been prepared in the crystalline form by Deville (*Compt. rend.*, 53, 163). Ebelmen (*Ann. Chim. Phys.* [3], 30, 349) obtained a black powder approximating in composition to a sesquioxide.

*Gelatinous Modification of Titanic Acid.*—This modification can be prepared by fusing titanic acid with potassium carbonate, washing the fused mass with water until the alkaline reaction has disappeared, and then treating the mass with hydrochloric acid (of about 35 per cent.) without heating. The liquid is filtered, and the filtrate on being allowed to stand for a time gelatinises. This fact was observed by H. Rose (*Gilb. Annal.*, 1823, 73—76), but appears to have been overlooked, as it is not mentioned in the text-books. A. J. G.

*Note.*—Gelatinous titanic acid was described by Graham (*Chem. Soc. J.*, 15, 256, and 17, 325).—A. J. G.

**Relation between Luteo- and Roseo-salts.** By S. M. JÖRGENSEN (*J. pr. Chem.* [2], 29, 409—422).—In former researches, the author has shown that the luteo-chromium and luteo-cobalt salts are analogous. In this paper he shows that the luteo-salts of cobalt and chromium correspond completely with the roseo-salts of cobalt, chromium, and rhodium, only that the former contain  $2NH_3$ , where the latter have  $2OH_2$ . In a table of the numerous luteo- and roseo-salts and double salts which the author has examined, it is seen that out of 45 luteo-salts only 5 contain more  $OH_2$  than is expressed by the above ratio, and that in 44 roseo-salts none contain less.

The following are a few out of the numerous examples given:—

Luteo-salt—			
$\text{Co}_2\text{12NH}_3(\text{NO}_3)_6$	$\text{Cr}_2\text{12NH}_3(\text{NO}_3)_6$	—	
Roseo-salt—			
$\text{Co}_2\text{10NH}_3(\text{NO}_3)_6\cdot 2\text{OH}_2$	$\text{Cr}_2\text{10NH}_3(\text{NO}_3)_6\cdot 2\text{OH}_2$	$\text{Rh}_2\text{10NH}_3(\text{NO}_3)_6\cdot 2\text{OH}_2$	
Luteo-salt—			
$\text{Co}_2\text{12NH}_3\cdot 6\text{HgCl}_2\cdot 2\text{OH}_2$	$\text{Cr}_2\text{12NH}_3\cdot 6\text{HgCl}_2\cdot 2\text{OH}_2$	—	
Roseo-salt—			
$\text{Co}_2\text{10NH}_3\cdot 6\text{HgCl}_2\cdot 4\text{OH}_2$	$\text{Cr}_2\text{10NH}_3\cdot 6\text{HgCl}_2\cdot 4\text{OH}_2$	—	
Luteo-salt—			
$\text{Co}_2\text{12NH}_3\cdot \left\{ \begin{smallmatrix} \text{I}_2 \\ 2\text{SO}_4 \end{smallmatrix} \right.$	$\text{Cr}_2\text{12NH}_3\cdot \left\{ \begin{smallmatrix} \text{I}_2 \\ 2\text{SO}_4 \end{smallmatrix} \right.$	—	
Roseo-salt—			
$\text{Co}_2\text{10NH}_3\cdot \left\{ \begin{smallmatrix} \text{I}_2 \\ 2\text{SO}_4 \end{smallmatrix} \right.\cdot 2\text{OH}_2$	—	$\text{Rh}_2\text{10NH}_3\cdot \left\{ \begin{smallmatrix} \text{I}_2 \\ 2\text{SO}_4 \end{smallmatrix} \right.\cdot 2\text{OH}_2$	
Luteo-salt—			
$\text{Co}_2\text{12NH}_3\cdot \text{Co}_2\text{Cy}_{12}$	$\text{Cr}_2\text{12NH}_3\cdot \text{Co}_2\text{Cy}_{12}$		
Roseo-salt—			
$\text{Co}_2\text{10NH}_3\cdot \text{Co}_2\text{Cy}_{12}\cdot 2\text{OH}_2$	$\text{Cr}_2\text{10NH}_3\cdot \text{Co}_2\text{Cy}_{12}\cdot 2\text{OH}_2$	$\text{Rh}_2\text{10NH}_3\cdot \text{Co}_2\text{Cy}_{12}\cdot 2\text{OH}_2$	
The following are two of the five exceptions:—			
Luteo-salt—			
$\text{Co}_2\text{12NH}_3\cdot 3\text{SO}_4\cdot 5\text{OH}_2$	$\text{Cr}_2\text{12NH}_3\cdot 3\text{SO}_4\cdot 5\text{OH}_2$	—	
Roseo-salt—			
$\text{Co}_2\text{10NH}_3\cdot 3\text{SO}_4\cdot 5\text{OH}_2$	$\text{Cr}_2\text{10NH}_3\cdot 3\text{SO}_4\cdot 5\text{OH}_2$	$\text{Rh}_2\text{10NH}_3\cdot 3\text{SO}_4\cdot 5\text{OH}_2$	

The analogy thus shown to exist between the luteo- and roseo-salts of cobalt, chromium, and rhodium is not confined to their composition, but holds as regards their solubilities, crystalline properties, and their appearance, formation, and changes. It is only therefore by their colour and nitrogen-estimations that the corresponding salts can be distinguished. As  $2\text{NH}_3 = 34$ , and  $2\text{OH}_2 = 36$ , the percentage of metal is almost the same in the two series. In many cases the roseo-salts do not lose the 2 mols.  $\text{OH}_2$  which are part of their constitution, without a deeper decomposition, but if they do, purpureo-salts are formed. These properties enabled the author to confirm the results of other authors.

The author describes the crystalline forms of the various salts, showing that the corresponding salts of each series have the same form. Thus the nitrate-sulphates, bromo-sulphates, and iodo-sulphates of luteo-chromium and luteo-cobalt, and roseo-chromium and roseo-cobalt, all crystallise in regular octohedrons, and the sodium pyrophosphate and sulphato-platinochloride double salts crystallise alike in bright regular six-sided plates. The platinobromides ( $3\text{PtBr}_4$ ) of luteo-chromium and roseo-cobalt form copper-coloured precipitates of quadratic or eight-sided plates. The platinobromides ( $2\text{PtBr}_4$ ) of luteo-cobalt and roseo-cobalt are indistinguishable, both forming long bright four- or six-sided needles, having the appearance of crystals of chromic anhydride. The mercurio-chlorides ( $6\text{HgCl}_2$ ) in all cases form long narrow four- or six-sided needles. The ferricyanides and cobalticyanides of roseo-cobalt, roseo-chromium, and

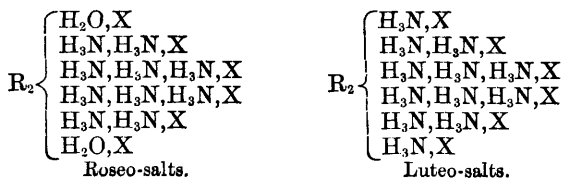
roseo-rhodium cannot be distinguished under the microscope from the corresponding luteo-cobalt and luteo-chromium salts. The auro-bromo-sulphates of roseo-cobalt, roseo-chromium, roseo-rhodium, luteo-cobalt, and luteo-chromium show dichroism, the colours being deep violet-blue and bright olive-green. The auro-chloro-sulphates of luteo-cobalt and roseo-cobalt are also, but in a much smaller degree, dichroic. If the nitrates of luteo-chromium or luteo-cobalt in dilute solution are precipitated by concentrated nitric acid, they crystallise in long narrow needles; if in concentrated solution by dilute nitric acid, they crystallise in quadratic plates or pyramids. The roseo-salts behave in a precisely similar way, only that in the roseo-chromium and roseo-cobalt salts the prism form predominates; in the roseo-rhodium salts, the plate form.

The luteo- and roseo-salts also resemble each other in their formation, and the author has already shown this (*J. pr. Chem.*, **23**, 229). The most convenient way to prepare roseo-salts is to treat the purpureo-salt with alkalis, such as silver oxide and water, or soda, or dilute ammonia. By using concentrated ammonia and taking precautions to prevent evaporation, luteo-salts are formed, as Mills has shown (*Phil. Mag.* [4], **35**, 245).

On treating purpureo-haloid salts with the haloïd acids, the corresponding purpureo-salts are formed. This property does not belong to the luteo-cobalt haloïd salts, but is possessed by the luteo-chromium salts. Luteo-chromic chloride, even with cold concentrated hydrochloric acid, forms chloropurpureo-chromic chloride. The bromide changes in the same way, more slowly with hydrobromic acid, but the action of hydriodic acid on the iodide is very slight. The author enumerates numerous other points in which the two series of salts agree. For example, many luteo- and roseo-salts are precipitated by acids with complete double decomposition (in contradistinction to the purpureo-salts); both luteo- and roseo-sulphates are capable of forming double salts, in which  $\text{ISO}_4$  is replaced by  $2\text{NO}_3$ ,  $2\text{Cl}$ ,  $2\text{Br}$ ,  $1\text{PtCl}_6$ ,  $1\text{PtBr}_6$ ,  $2\text{AuCl}_4$ , or  $2\text{AuBr}_4$ ; both luteo- and roseo-nitrates form double salts, in which  $4\text{NO}_3$  are replaced by  $2\text{PtCl}_6$ ; both luteo- and roseo-chlorides form double salts with  $2\text{HgCl}_2$  and  $6\text{HgCl}_2$ ; and both form three double salts with platinic chloride containing 1, 2, or 3  $\text{PtCl}_4$ .

The chief difference in properties between roseo- and luteo-salts is that roseo-salts (when not combined with mercuric chloride, platinic chloride, &c.) are dissolved by ammonia with formation of basic salts. Luteo-salts are not decomposed by ammonia, and are less soluble in it than in water.

The author proposes the following structural formulæ for these salts:—



In these formulæ  $\text{H}_2\text{O}^{\text{iv}}$  has the same function as  $\text{H}_3\text{N}^{\text{v}}$ . The luteo-salts are therefore primary amines, the purpureo-salts partly primary amines and partly metallic salts, and the roseo-salts partly primary amines and partly primary *oxines*, that is, compounds containing tetrad oxygen, corresponding to the sulphur in the sulphines. The author states the grounds on which he bases this.

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A. B.

## Mineralogical Chemistry.

**Elasticity of Crystals of the Regular System.** By K. R. KOCH (*Jahrb. f. Min.*, 1884, 2, Ref., 156).—The author has already determined the coefficients of elasticity of rock salt; he has now extended his observations to sylvine and sodium chlorate. The final results are—

	$E_1$ .	$E_2$ .	$\frac{E_1}{E_2}$ .
KCl .....	4010	2088	1.92
NaCl .....	4030	3395	1.19
NaClO <sub>3</sub> .....	4047	3190	1.27

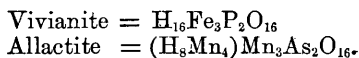
The coefficients  $E_1$  and  $E_2$  are expressed in  $\frac{\text{kilogram}}{\text{square mm.}}$ .  $E_1$  was determined from the deflection of rods, the longitudinal axis of which was perpendicular to the face of the cube,  $E_2$  from rods perpendicular to the face of the dodecahedron. The results in the case of NaClO<sub>3</sub> are only provisional; those for sylvine, on the other hand, are exact to 0.5 per cent., from numerous observations on 15 rods from three crystals, so that the author concludes that the coefficient of elasticity of sylvine for a given direction is always the same. B. H. B.

**Dilatation of Crystals on Change of Temperature.** By L. FLETCHER (*Jahrb. f. Min.*, 1884, 2, Ref., 153—154).—With the view of testing the author's theory of the possible want of permanency of the thermic axes, Beckenkamp made measurements of the angles of anorthite, axinite, and orthoclase at temperatures of 20°, 80°, 140°, and 200°. From these measurements he deduced the positions of the thermic axes. He found that, whilst the variation in the case of axinite and orthoclase is within the limit of experimental errors, in the case of anorthite, the axis of minimum expansion for 20—80° forms an angle of 26 $\frac{1}{2}$ ° with the corresponding axis for 20—200°. An examination undertaken by the author to test this remarkable result shows it to be due to experimental error. B. H. B.

**Isomorphous Minerals which are not Chemically Analogous.** By C. RAMMELSBURG (*Jahrb. f. Min.*, 1884, 2, Mem., 67—74).—Among minerals, especially among silicates, groups occur, the members of which have the same or nearly the same crystalline form, or, in other words, are isomorphous. Their constitution in some instances is perfectly analogous, whilst in others this is not the case. The latter are

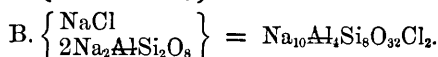
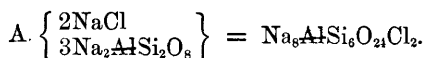
of special interest, as it is usually thought that isomorphous bodies must have an analogous constitution, or, in fact, that analogous constitution is the basis of isomorphism. To the silicate groups, the members of which have an analogous constitution, belong the olivine group; the augite group, the garnet group, the tourmaline group, and the group comprising epidote and vesuvian. Silicate groups, however, exist in which, notwithstanding the similar form, the constitution is not analogous. In the feldspar group the difference extends from the mono- to the tri-silicates. By Tschermak's law, the nature of the lime-soda feldspars is rendered clear. From the ratio  $Al : Si$  may be deduced that of  $Na : Ca$ . The two members are known from the molecular mixture of which each intermediate member is produced. It is thus shown that silicates, the constitution of which is not analogous, can be isomorphous. In the mica group, the members of which have certainly one and the same form, the constitution varies to a small extent. They are partly dibasic silicates, and partly combinations of the latter with normal silicates. The preceding remarks are supported by examinations of the groups of scapolite, chabasite and phillipsite, and they tend at the same time to show how certain chemical ideas are entirely misunderstood by many mineralogists.

Sjögren has recently described a manganese arsenate from Nordmarken, which he calls allactite, and which has the form of vivianite and cobalt-bloom, but contains 4 mols. less  $H_2O$  and 4  $MnO$  more. Instead of writing  $\left\{ \begin{matrix} Mn_3As_2O_8 \\ 4MnH_2O_2 \end{matrix} \right\}$ , he represents the 4 $MnO$  as replacing 4 $H_2O$ , in order to explain the isomorphism by analogy. He should properly have written—



Forty years ago Hermann enunciated the law that among isomorphous compounds not of analogous constitution there are always two terminal members, from the mixture of which, in various proportions, all the others are produced. This theory has never been largely adopted, as it is based on hypotheses which cannot be proved by experiment. Tschermak's law, however, is of great scientific value, and it would not be less important to prove similar laws for other groups in which similar form is accompanied by dissimilar constitution. For this purpose, it would, however, be necessary for the two terminal members to be actually known. Unfortunately Tschermak himself, in a memoir recently published, regards the minerals belonging to the scapolite series as mixtures of two terminal members—a lime-alumina silicate and a soda-alumina silicate. The former he calls meionite-silicate,  $Ca_4Al_3Si_6O_{25}$ , and regards it as a combination of 5 mols. dibasic with 1 mol. tribasic silicate. This compound has not yet been discovered, as meionite itself contains a certain amount of the second terminal member, which he calls marialite-silicate, and regards as a compound of  $2NaCl + 3(Na_2AlSi_6O_{16})$ , in which the second member has the formula of albite. As he adopts the formula  $Na_3Al_3Si_{18}O_{48}Cl_2$ , he assumes that the O is replaced by  $Cl_2$ . If the silicate and chloride

compounds are regarded in this way, the following results are obtained for sodalite :—



In other words, the sodalites A (Greenland, Ischia, Salem, Litchfield, Vesuvius) consist, like the meionite-silicate, of 5 mols. bibasic and 1 mol. tribasic silicate, whilst the sodalites B (Ditro, Bolivia) must contain 7 and 1 mol. respectively. The formula of apatite transposed in the same way would no longer represent a phosphate. All scapolites too must contain chlorine, which is not the case. The marialite mixture containing 4·2 per cent. chlorine is, however, up to the present time merely hypothetical. In just the same way, Fresenius traced the members of the phillipsite group from two terminal members, one of which is desmine and the other an hypothetical hydrate of the anorthite mixture. Still more arbitrary is his theory of two such terminal members in the chabasite group, as neither of them have, up to the present time, been shown to exist.

B. H. B.

**Mineralogical Notes.** By V. v. ZEPHAROVICH (*Jahrb. f. Min.*, 1884, 2, Ref., 157—159).—The author gives an account of several new and interesting occurrences of minerals at localities in the Tyrol, formerly unknown in this respect. The minerals from the Zillergrund described are: harmotome, scolecite and adularia, desmine, and calcite. The minerals from the Stillapp Valley are: apatite, pericline, titanite, rutile, and laumontite.

B. H. B.

**Sulphur from the Fumaroles of Montecito in the Island of Ischia.** By A. OGLIOLO (Gazetta, 14, 30—31).—During the observations which the author made on the gaseous emanations of Ischia, he noticed in the fumarole of Montecito, near Casamicciolo, some prismatic crystals of sulphur, apparently monoclinic, amongst those of the ordinary trimetric form. On making careful search in the same neighbourhood, he found some magnificent prismatic crystals of sulphur but little coloured and quite transparent; some of them 5 mm. long. He has submitted them to Scacchi for crystallographic measurement.

C. E. G.

**Cobalt-, Nickel-, and Iron-Pyrites.** By L. W. MCCAY (*Jahrb. f. Min.*, 1884, 2, Ref., 161—163).—*Safflorite* from Schneeberg gave on analysis the following results :—

As.	S.	Ni.	Co.	Fe.	Bi.	Total.
66·33	0·16	27·76	0·64	trace	5·11	100·00

The radiated fibrous safflorite from Wolfgang Maasen, near Schneeberg, gave the following analytical results :—

As.	S.	Co.	Fe.	Ni.	Cu.	Bi.	Quartz.	Total.	Sp. gr.
65·02	0·49	16·00	11·20	trace	0·65	0·37	5·82	99·55	7·28



The safflorite from Bieber, the spathiopyrite of Sandberger (Abstr., 1884, 405) gave :—

As.	S.	Co.	Fe.	Ni.	Bi.	Cu.	Total.	Sp. gr.
68·27	1·30	13·12	14·38	1·88	1·24	0·26	100·45	7·26

From the author's investigations, it is clear that there is a rhombic modification of smaltine which only approaches to the formula  $RAs_2$ . The compact grey ferruginous and heavy varieties must also be regarded as rhombic modifications of smaltine. This rhombic modification was discovered by Breithaupt, whose name "safflorite" should consequently be retained.

*Cheleutite*.—This name was given by Breithaupt to bismuth-cobalt ore. The analyses of two specimens from Schneeberg gave :—

	As.	S.	Co.	Fe.	Ni.	Cu.	Bi.
I.	75·09	1·30	12·46	5·16	3·01	1·58	0·78
II.	45·30	1·10	8·42	3·08	2·18	0·72	trace

	Quartz.	Total.	Sp. gr.
I.	0·42	99·80	6·30
II.	39·00	99·80	6·35

The author is of opinion that the mineral, which in composition and properties resembles skutterudite, does not belong to this species but to smaltine, as its specific gravity is so low. Under all circumstances, the name bismuth-cobalt ore must be dropped. If it is to have a special name, Breithaupt's name, cheleutite, is to be preferred.

*Chloanthite from Schneeberg*.—A specimen of ore described in the Freiberg collection as safflorite proved to be chloanthite, with the following composition :—

As.	S.	Ni.	Co.	Fe.	Bi.	Total.
68·40	1·06	24·95	4·20	0·69	0·21	99·51

The analysis of chloanthite from Schneeberg gave :—

As.	S.	Ni.	Co.	Fe.	Cu.	Total.	Sp. gr.
75·40	0·73	11·90	3·42	7·50	0·39	99·34	6·54

Formula  $R_2S_5$ .

*Radiated mispickel*, from Orawitza, formerly regarded by Breithaupt as glaucodote, and by Tschermak as allocase, has the following composition :—

As.	S.	Fe.	Co + Ni.	Total.	Sp. gr.
45·19	19·80	33·60	1·40	99·99	6·05

*Cobaltine from Schladming*.—

As.	S.	Co.	Fe.	Ni.	Au.	Total.
43·12	18·73	29·20	5·30	3·20	trace	99·55

*Arsenical pyrites from Hüttenberg* (Hüttenbergite).—After the

removal of 1·70 per cent. of bismuth, the following analytical results were obtained :—

As.	S.	Fe.	Total.	Sp. gr.
68·87	1·09	29·20	99·16	6·75

*Smaltine from Schneeberg.*—

As.	S.	Co.	Fe.	Ni.	Cu.	Total.	Sp. gr.
71·53	1·38	18·07	7·31	1·02	0·01	99·32	5·466

*Geierite from Breitenbrunn* ( $7\text{FeS}_2 + 6\text{Fe}_3\text{As}_2$ ).—

As.	S.	Fe.	Sp. gr.
61·40	6·73	31·20	31·20

*Mispickel from Queropulca in Peru.*—

As.	S.	Fe.	Cu.	Total.	Sp. gr.
42·54	20·96	35·03	0·47	99·00	6·069

B. H. B.

**Mispickel from Auerbach.** By G. MAGEL (*Jahrb. f. Min.*, 1884, 2, Ref., 166—168).—In the granular limestone of Auerbach, three different types of mispickel occur. The crystals belonging to type I are of rather frequent occurrence. They attain a size of 1—4 mm., sometimes 5—9 mm., and exhibit the usual simple forms of mispickel :  $\infty\text{P}$ ,  $\frac{1}{4}\dot{\text{P}}\infty$ ,  $\dot{\text{P}}\infty$ . Of these  $\frac{1}{4}\dot{\text{P}}\infty$  predominates. The analysis gave the following percentage composition :—

S.	Fe.
20·339	35·812

Cleavage  $\infty\text{P}$ .

The crystals belonging to type II are extremely rare. They attain a size of 3—5 mm., sometimes 6—9 mm., and are columnar. The faces observed were the following :  $\infty\text{P}$ ,  $\frac{1}{2}\dot{\text{P}}\infty$ ,  $\dot{\text{P}}\infty$ ,  $\dot{\text{P}}2$ ,  $\dot{\text{P}}\infty$ ,  $2\dot{\text{P}}\infty$ , and the new face  $\frac{2}{3}\dot{\text{P}}\infty$ . Cleavage along  $\infty\text{P}$  could not be observed ; distinct basal cleavage. The mean of two analyses gave :—

S.	As.	Fe.	Total.
19·911	44·106	35·041	99·058

The mispickel of types I and II agree very well with the series of Arzruni and Baerwald (*Abstr.*, 1884, 404) :—

	Axis $a$ .	S found.	S calculated.
Mispickel from Ehrenfriedersdorf...	0·67811	19·761	19·748
„ Auerbach (type II) ..	0·67830	19·911	19·794
Plinian .....	0·67960	20·080	20·099
Mispickel from Sala.....	0·68066	20·410	20·351
„ Auerbach (type I)....	0·68185	20·639	20·530
„ Joachimsthal.....	0·68215	20·520	20·701

Type III is, unfortunately, only represented by a single specimen.

To two crystals crossing along  $\bar{P}\infty$ , a third is added according to the same law, forming a drilling. The crystals exhibit the faces  $\frac{1}{2}P\infty$ ,  $\bar{P}\infty$ ,  $\infty P$ .  
B. H. B.

**Crystallised Voltzine.** By G. CESARO (*Jahrb. f. Min.*, 1884, 2, Ref., 166).—On the surface of a mixture of blende and galena, the author found crystals resembling radiated antimony glance needles. They are flat, compressed, rectangular needles, bounded above by rhombic octahedra, translucent, of a pale orange colour, and with waxy lustre. The physical and chemical properties are those of blende, except that the crystals contain rather less sulphur. The author supposes that the mineral is either a pseudomorph of blende after antimony glance, or, as is more probable, crystallised voltzine.  
B. H. B.

**Occurrence of Iron in Mexico.** (*Dingl. polyt. J.*, 252, 527).—In the province of Durango, the so-called Cerro de Mercado iron mountain occurs, which is 1100 m. long, 335 m. wide, and 195 m. high, and represents a mass of about 200 million tons of ore. The ore which exists under this mountain is said to contain more iron than the quantity obtained in England during 350 years. The following analysis gives the average composition of this ore:—

$Fe_3O_4$ .	FeO.	MnO.	$TiO_2$ .	CaO.	MgO.	$SO_3$ .
2.071	77.571	0.113	0.710	5.050	6.364	0.212
	$P_2O_5$ .	$SiO_2$ .	Loss on ignition.	Other ingredients.		
	3.041	7.760	1.984	1.124		

The pig iron produced from this ore contained 0.771 per cent. silicon, 0.428 per cent. sulphur; the bar iron showed 0.105 per cent. silicon and 0.193 per cent. phosphorus.  
D. B.

**Pitchblende and Xenotime from Norway.** By W. C. BRÖGGER (*Jahrb. f. Min.*, 1884, 2, Ref., 170—171).—*Pitchblende from Moss*.—The forms observed were: O, and  $\infty O$ . Colour black; streak greenish-black. H. = 6. Sp. gr. 9.03. The analysis gave the following results:—

$SiO_2$ .	$UO_3$ .	$UO_2$ .	PbO.	FeO.	CaO.	$H_2O$ .	Total.
0.31	38.23	50.42	9.72	0.25	0.21	0.70	99.84

corresponding with the formula  $R_5O_{12} = 3RO_2 + 2RO_3$ .

*Xenotime* occurs frequently in many pegmatite veins in various parts of Norway. The occurrence at Narestö, near Arendal, is especially remarkable. It there forms aggregates on chloritic magnesia mica. The dark brown crystals exhibit the forms  $P$ ,  $\infty P$ ,  $3P3$ . Xenotime may easily be distinguished from monazite, which accompanies it, by its prismatic cleavage. The character of the double refraction of xenotime is positive.  
B. H. B.

**A Uranium Mineral from Moss, and on the Occurrence of Uranates Generally.** By C. W. BLOMSTRAND (*J. pr. Chem.* [2] **29**, 191—228).—The mineral, which was found at Änneröd, in the vicinity of Moss in Norway, is iron-black in colour, sp. gr. 8·73, hardness 5—6. Fracture, splintery. The following results were obtained on analysis:—

U <sub>3</sub> O <sub>8</sub> .	SiO <sub>2</sub> .	PbO.	ThO.	CeO.	YO.	FeO.	CaO.	H <sub>2</sub> O.
80·97	0·81	8·41	5·64	0·38	2·42	1·26	0·30	0·83 = 101·02

The mineral, which has been named bröggerite by the author, is closely related to cleveite. The author points out that, according to our present knowledge, the natural uranates, of which pitchblende may be taken as the type, are built up according to the formula  $3\text{RO}, \text{UO}_3$ , in which the uranic oxide uniformly appears as an ortho-acid, whilst the basic portion of the molecule is principally composed of uranous oxide, the latter being, however, always partially replaced by lead or some kindred metal. For true pitchblende or uranine the most probable formula is shown to be  $7\text{UO}_2, \text{PbO}, 5\text{UO}_2 = \text{U}_7\text{Pb}(\text{UO})_5$  or  $\text{UPbO}_6\text{U} + 2\text{U}_3(\text{O}_6\text{U})_3$ . Of the thoruranines there are two forms known—(1) bröggerite, for which the formulæ  $\text{UO}_2, \text{RO}, \text{UO}_3 = \text{URO}_6\text{U}$ , or  $6\text{URO}_6\text{U} + \text{U}_3(\text{O}_6\text{U})_2$  are suggested; and (2) cleveite,  $\text{UO}_2, 4\text{RO}, 2\text{UO}_3 + 4\text{aq} = \text{UR}_4(\text{O}_6\text{U})_2 + 4\text{aq}$ . P. F. F.

**Herderite.** By A. WEISBACH (*Jahrb. f. Min.*, 1884, **2**, Mem., 134—136).—The analysis of a specimen of herderite from Ehrenfriedersdorf, in the collection of the Freiberg School of Mines, gave the following results:—(I.) The results obtained by Hidden in the analysis of herderite from Stoneham, Oxford Co., Maine (*Abstr.*, 1884, 827), are added (II.)—

	CaO.	Be <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	Loss.
I.	34·06	8·61	6·58	1·77	42·44	6·54
II.	33·21	15·76	—	—	44·31	6·72

The herderite from Stoneham has also been analysed for the author by Winkler, who found in 101·7 mgrms.—

CaO.	Be <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.	Total.
33·67	14·84	2·26	1·18	41·51	6·59	100·05

For the substance free from aluminium and iron the formula would be:  $\text{Ca}_6\text{Be}_4\text{P}_6\text{O}_{27} + 4\text{H}_2\text{O}$ , demanding—

CaO.	Be <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.
34·13	15·34	43·23	7·30

B. H. B.

**Richellite, a New Mineral Species.** By G. CESARO and G. DESPRET (*Jahrb. f. Min.*, 1884, **2**, Ref., 179).—At Richelle, near Visé, a mineral occurs which has the following composition:—

P <sub>2</sub> O <sub>5</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	H <sub>2</sub> O.	HF.	Total.
28·78	28·71	1·81	5·76	29·43	6·11	100·60

On heating it, the substance suddenly gave off fumes of hydrofluoric acid, changing from its original bright yellow colour to a brownish-red, and no longer contained any fluorine. The authors, therefore, conclude that fluorine was not present as CaF<sub>2</sub>. The mineral, formerly regarded as a variety of delvauxite, is, therefore, new. It forms bright yellow masses, with resinous lustre. H. = 2—3. Sp. gr. 2. Its tenacity is very weak. The water given up at 100° (23·33 per cent.) is free from hydrofluoric acid. Before the blowpipe, it fuses easily to a black, slightly magnetic enamel. It is easily soluble in acids, and gives a distinct fluorine reaction. The mineral is associated with halloisite, allophane, and a greenish iron phosphate. The authors calculate from their analyses that richellite contains 2 mols. P<sub>2</sub>O<sub>5</sub>, 2 mols. R<sub>2</sub>O<sub>3</sub>, 1 mol. CaO, 3 mols. HF, and 16·6 mols. H<sub>2</sub>O, and they are of opinion that the fluorine is combined with iron.

B. H. B.

**Natural Hydrous Double Sulphates.** By J. BLAAS (*Jahrb. f. Min.*, 1884, 2, Ref., 163—165).—In the neighbourhood of Madeni Zakh, in Persia, the hydrous double sulphates, voltaite, metavoltine, and botryogen occur as decomposition-products of a trachytic rock containing iron pyrites.

*Voltaite*.—The crystals appear to be regular, with the combination O, ∞O∞, ∞O, mOm. Colour greenish-black. Streak greyish-green. Fracture conchoidal. Greasy lustre. Brittle. H. = 2—3. Sp. gr. 2·6. Soluble with difficulty in cold water. The analysis gave the following results:—

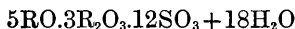
SO <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
49·12	13·85	3·72	5·24	7·35	2·37	1·62	16·60	99·87

Formula 3Al<sub>2</sub>O<sub>3</sub>.7Fe<sub>2</sub>O<sub>3</sub>. This analysis does not exactly agree with the analyses of voltaite by Abich and Tschermak.

*Metavoltine*.—System hexagonal. Colour sulphur-yellow. H. = 2·5. Sp. gr. 2·53. The analysis gave the following results:—

SO <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
46·90	21·20	2·92	9·87	4·65	14·58	100·12

Molecular proportion of SO<sub>3</sub> : Fe<sub>2</sub>O<sub>3</sub> : RO : H<sub>2</sub>O = 13 : 3 : 5 : 18; RO being 3FeO, 7K<sub>2</sub>O, 5Na<sub>2</sub>O. From this the formula



is deduced.

*Botryogen* forms compact, crystalline masses of brownish-violet colour and glassy lustre. Streak violet-white, brittle, transparent in thin plates. H. = 2·5. Sp. gr. 2·138. Soluble in cold water to a brownish-violet solution. On the addition of sulphuric acid the colour disappears. The analysis gave:—

SO <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	H <sub>2</sub> O.	Total.
40·95	20·50	4·12	3·59	30·82	99·98

Formula RSO<sub>4</sub> + Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + 13H<sub>2</sub>O, in which R = 5Fe, 7Mg.

This analysis agrees with the composition of roemerite, except that in the latter R is replaced by  $2\text{Zn}, 7\text{Fe}$ , and that the percentage of  $\text{H}_2\text{O}$  is also rather smaller. The author consequently regards botryogen and roemerite as identical.

B. H. B.

**Conversion of Rutile into Ilmenite.** By A. V. LASAULX (*Jahrb. f. Min.*, 1884, 2, Ref., 165—166).—The author describes the pseudo-morphs of titanite iron after rutile from Vannes. The alteration begins by the addition of  $\text{FeO}$ , and the separation of  $\text{FeTiO}_3$ , more  $\text{FeO}$  subsequently enters the isomorphous mixture with the  $\text{FeTiO}_3$ , and titanite iron is finally formed containing more  $\text{Fe}_2\text{O}_3$  than  $\text{FeO}$ . The author supposes that  $\text{FeTiO}_3$  is replaced by  $\text{Fe}_2\text{O}_3$ , and that every variety of titanite iron could be formed in this way. He therefore regards all titanite iron produced in the same way from rutile as isomorphous mixtures of  $m(\text{FeTiO}_3)$  and  $n(\text{Fe}_2\text{O}_3)$ , and not as mixtures of  $\text{Fe}_2\text{O}_3, \text{Ti}_2\text{O}_3$ . Probably, two varieties of titanite iron must be distinguished: (1) original  $(\text{FeTi})_2\text{O}_3$ ; and (2)  $\text{FeTiO}_3$ , of undetermined crystalline form, originating from rutile.

B. H. B.

**Melanophlogite.** By G. SPEZIA (*Jahrb. f. Min.*, 1884, 2, Ref., 177—178).—Minute cubes and crystalline aggregates of melanophlogite occur implanted on a thin coating of opal covering sulphur crystals from Sicily. The cubes become black on the surface when heated. This black colour is due to carbon. Melanophlogite also occurs, like the opal, covering sulphur crystals, or in the form of small stalactites; an analysis of the latter form was made with 0.1196 gram, the results being as follows:—

$\text{SiO}_2$ .	$\text{SO}_3$ .	C.	$\text{Fe}_2\text{O}_3$ .	Loss on ignition.
89.46	5.60	1.33	0.25	2.42

B. H. B.

**The Felspars of Pantelleria.** By H. FÖRSTNER (*Jahrb. f. Min.*, 1884, 2, Ref., 171—176).—The volcanic island of Pantelleria consists of (1) phonolites and liparites in beds; (2) rocks of the oldest crater, consisting of older and more recent augite-andesites; (3) rock of the most active period of eruption; pantellerite, a dacite-like rock with triclinic feldspar. Most of the feldspars described are from this rock. (4) Rock of the most recent craters, feldspar-basalt. The trachytic rocks of the island are very rich in feldspar. The feldspar crystals frequently separate out by weathering. Among these, orthoclase crystals are rare; they all have a larger percentage of sodium than usual, whilst a larger percentage of potassium is met with in the plagioclase. The paper gives elaborate details of the crystallographic and optical characters of the following feldspars: (1) monoclinic feldspar (soda orthoclase) from the white liparite of the Lake Bagno dell' Aqua, and from Cala Porticello; (2) triclinic feldspars (microcline albite series). These occur in the rocks which are more recent than liparite, and which contain no orthoclase. The feldspars described in detail are plagioclase from the older augite-andesite, plagioclase from the augite-andesite lava, and plagioclase from the pantellerite lava.

B. H. B.

**Rubellan.** By M. W. HOLLRUNG (*Jahrb. f. Min.*, 1884, 2, Ref., 168—170).—The crystals of rubellan from the basalt-lava of the Laacher See are of a reddish-brown colour, and variable in their physical properties. Sp. gr. 2.50—2.86. They cleave easily in one direction, and all are optically biaxial. The microscopic examination shows that rubellan is not a purely homogeneous substance, but contains inclusions of various kinds. The chemical analysis of three specimens gave the following results:—

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	35.90	0.65	15.34	27.69	3.24	11.31	1.59	1.38	3.31	100.41
II.	36.97	0.80	17.94	22.81	1.50	11.97	1.60	1.42	3.61	98.62
III.	37.09	1.24	17.02	25.96	1.19	11.53	2.01	0.38	4.66	101.08

Hot hydrochloric acid, after 15 hours' action, dissolved:—

	I.	III.
Al <sub>2</sub> O <sub>3</sub> .....	14.83 per cent.	17.74 per cent.
Fe <sub>2</sub> O <sub>3</sub> .....	30.18     ,,	22.31     ,,
MgO.....	12.13     ,,	11.61     ,,

The mica substance always contained a quantity of iron-ochre. A constitutional formula cannot be calculated for rubellan, as it is not homogeneous, but merely an alteration-product of mica or augite.

B. H. B.

**Synthesis of Pyroxene.** By C. DOELTER (*Jahrb. f. Min.*, 1884, 2, Mem., 51—66).—The assumption by silicates of the form  $R'R''_2SiO_6$  explains very satisfactorily the complicated constitution of the pyroxenes, and has, on that account, been largely adopted. No exact evidence for it, however, exists. It is of interest, therefore, to investigate experimentally the question whether, by fusing together diopside and Al<sub>2</sub>O<sub>3</sub> or Fe<sub>2</sub>O<sub>3</sub>, pyroxenes may be obtained, the constitution of which cannot be explained by the assumption of the silicate  $R''O, R'''_2O_3, SiO_2$ , and, secondly, to find out whether these silicates crystallise, and whether they agree with pyroxene. All the experiments were effected in a Leclercq-Forquignon furnace in platinum crucibles with 4—6 grams of the substance. The result of the experiments was that the silicates  $R''O, R'''_2O_3, SiO_2$ , which have, up to the present time, been regarded as purely hypothetical compounds, crystallise and exactly resemble in their properties the augites produced by the fusion of natural augites. With the exception of the solubility, which is generally greater than that of the augites produced in nature, these artificial products perfectly coincide with the natural augites, and consequently the theory, according to which such silicates are actually present in these natural augites, receives renewed support.

B. H. B.

**Hydrated Double Silicate of Zinc and Aluminium.** By G. CESARO (*Jahrb. f. Min.*, 1884, 2, Ref., 177).—The author found a new mineral on smithsonite of unknown locality. It formed fibrous lamellar masses of yellowish-white colour, which could be scratched with the finger nail, and could be separated into fibres like asbestos.

The mineral has a silky lustre, is fusible to a white enamel, and gelatinises with nitric acid. The analysis gave the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	ZnO.	CuO.	H <sub>2</sub> O.	CaO.	CO <sub>2</sub> .
20·1	13·9	47·0	trace	13·2	2·0	3·8
B. H. B.						

**Analysis of the Water of a Thermal Spring in the Island of Pantellaria.** By G. BRIGNONE (*Gazzetta*, 14, 42—54).

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## Organic Chemistry.

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**Hydrocarbons from American Petroleum and their Derivatives.** By G. LEMOINE (*Bull. Soc. Chim.*, **41**, 161—166).—Schorlemmer having isolated two isomeric octanes from American petroleum, the author has investigated the higher homologues in order to discover whether corresponding isomerides were present. The petroleum used in the investigation was a fraction obtained by distillation on the large scale, and having the mean density of the nonane studied by Pelouze and Cahours (0.74 at 15°). This liquid was submitted to a series of fractional distillations in Le Bel and Henninger's apparatus. The fractions were purified from olefines by treatment with bromine and subsequent distillation in a vacuum. The proportion of olefines present was about 30 per cent. The octane, nonane, and decane obtained in this way were substantially the liquids described by Pelouze and Cahours. Chlorine-derivatives of these hydrocarbons were obtained by the action of chlorine below 65°. The derivatives, after purification, were converted into the alcohols by heating them with alcoholic potassium acetate in sealed tubes at 156°. The acetate thus obtained was saponified with potash in the usual way, and the alcohol separated from the corresponding olefine by fractional distillation. The constants determined were boiling point, density, and vapour-density.

*Octane.*—This hydrocarbon and its derivatives have already been described by other investigators. In the present instance, the octane was isolated merely for the purposes of comparison. It was obtained by four distillations, and was not treated with bromine. B. p. 121° at 779 mm., 82° at 212 mm.; 63° at 110 mm., 31° at 27 mm. Pelouze and Cahours give 116—118° as the boiling point at ordinary pressures. The two octanes examined by Schorlemmer boiled at 119—122° and 122—125°. The density of the liquid was 0.732 at 12.1° (0.725 at 15°, Cahours). Vapour-density 4.03, determined at 179°. An analysis of the hydrocarbon showed that it contained 84.6 per cent. of carbon, 15.1 of hydrogen.

*Nonane.*—Prepared by seven distillations of the original petroleum and subsequent treatment with bromine, followed by five distillations

in a vacuum. B. p. 135—137°; sp. gr. 0·742 at 12·4° (0·741 at 15°, Cahours); vapour-density 4·59, determined at 180°. An isomeride was obtained by ten fractional distillations, followed by two successive treatments with bromine and five fractional distillations in a vacuum. B. p. 129·5—131·5°; sp. gr. 0·743 at 0°, 0·734 at 12·7°, 0·731 at 16°, 0·725 at 24·7° (0·741 at 15°, Cahours); vapour-density 4·47, determined at 190°.

*Monochlorononane*.—This was prepared from the second isomeride (b. p. about 132° at 759 mm.; sp. gr. 0·730 at 23·8). B. p. 180—184° (196° with partial decomposition, Cahours); sp. gr. 0·911 at 23·3°, 0·908 at 25·8 (0·899 at 15°, Cahours); vapour-density taken at 231·6° with partial decomposition, 5·94.

*Nonylic Alcohol*.—This was prepared from a nonane boiling between 130—135°. B. p. 186—189°. (The alcohol—b. p. 200°—examined by Pelouze and Cahours was prepared from nonane boiling at 136—138°). Sp. gr. 0·855 at 18·5°. An ultimate analysis gave C 75·7 per cent., H 13·3 per cent.

*Nonylene*.—This body was separated from the alcohol by fractional distillation. B. p. 133—136° (140° Wurtz); sp. gr. 0·853 at 18·4°. This olefine is isomeric with that obtained from metaoleic acid (b. p. 110°) by Fremy.

*Decane*.—Obtained by 15 fractional distillations of the petroleum, and purification of the liquid by bromine, followed by two distillations in a vacuum. B. p. 151—160° at 757 mm., 67·5° at 36 mm. (at the ordinary pressure 160°, Pelouze and Cahours; 155—157°, Wurtz; 155—160°, Cloëz); sp. gr. 0·764 at 0°, 0·753 at 15·6, 0·751 at 17°, 0·739 at about 35·5 (0·757 at 15°, Cahours; 0·760 at 15°, Cloëz); vapour-density 4·95, determined at 200·7°.

*Monochlorodecane*.—This was prepared from the decane just described (b. p. 155°). B. p. 201—203° (200—204°, Pelouze and Cahours); sp. gr. 0·908 at 19°.

*Decylene*.—Monochlorodecane, purified by three fractionations, was heated for 17 hours at about 110° with an excess of alcoholic potash. The product was treated with water, the hydrocarbon dried by calcium chloride, and rectified by distillation. B. p. 159—174° (158—160°, Pelouze and Cahours); sp. gr. 0·855 at 14°.

*Decylic Alcohol*.—This was prepared by the general method from monochlorodecane, and was separated from decylene by fractional distillation. After two rectifications, it boiled at about 200°. Sp. gr. 0·858 at 18·5°. A combustion gave C 76·1, H 14·2.

The author intends to verify and complete these results, using another specimen of petroleum. The hydrocarbons described above appear to be isomeric with those obtained by Krafft from the fatty acids.

W. R. D.

**Chlorine-derivatives of Dibromodinitromethane.** By S. N. LOSANITSCH (*Ber.*, 17, 848—849).—It has been shown previously that dibromodinitromethane reacts with alkaline hydroxides to form salts; thus  $\text{CBrK}(\text{NO}_2)_2$  is formed with potassium hydroxide (*Abstr.*, 1883, 564). Chlorine passed through an aqueous solution of this compound causes the separation of *chlorobromodinitromethane*,  $\text{CBrCl}(\text{NO}_2)_2$ , as

an oil. By the action of potash on this in alcoholic solution, the crystalline compound  $\text{CClK}(\text{NO}_2)_2$  is formed: by passing chlorine into its aqueous solution, it is converted into *dichlorodinitromethane*,  $\text{CCl}_2(\text{NO}_2)_2$ , an oily body, first described by Marignac. H. B.

**Higher Homologues of Acetylene.** By F. KRAFFT (*Ber.*, **17**, 1371—1377).—The author has previously described a number of higher members of the paraffin series (*Abstr.*, 1882, 1271), and of the olefine series (this vol., 572), prepared in a state of purity by synthetical methods. From the higher olefines he now obtains the corresponding members of the acetylene-group as follows:—The olefine is dissolved in several times its weight of carbon bisulphide, cooled by a freezing mixture, and one molecular proportion of bromine diluted with carbon bisulphide added slowly and with constant shaking. The resulting dibromide, after evaporation of the carbon bisulphide, is heated with alcoholic potash in open vessels, precipitated by water, and again heated with alcoholic potash in closed vessels for four to five hours at  $150^\circ$ . The acetylenes prepared in this way may be purified by two to three distillations under reduced pressure. They combine eagerly with bromine.

*Dodecylene dibromide*,  $\text{C}_{12}\text{H}_{24}\text{Br}_2$ , is a colourless liquid of faint odour, it can be solidified by means of liquid sulphurous anhydride, and then melts at  $-15^\circ$ . *Dodecylidene*,  $\text{C}_{12}\text{H}_{22}$ , is a colourless liquid, boils at  $105^\circ$  under 15 mm. pressure, and can be solidified by strong cooling, and then melts at  $-9^\circ$ . Its sp. gr., compared with water at  $4^\circ$ , is 0.8030 at  $0^\circ$ , 0.7917 at  $15^\circ$ , and 0.7788 at  $32.5^\circ$ .

*Tetradecylene bromide*,  $\text{C}_{14}\text{H}_{28}\text{Br}_2$ , melts at  $0^\circ$ . *Tetradecylidene*,  $\text{C}_{14}\text{H}_{26}$ , forms a crystalline mass, melts at  $+6.5^\circ$ , and boils at  $134^\circ$  under 15 mm. pressure. Sp. gr. = 0.8064 at  $6.5^\circ$ , 0.8000 at  $15.2^\circ$ , and 0.7892 at  $30^\circ$ .

*Cetene bromide*,  $\text{C}_{16}\text{H}_{32}\text{Br}_2$ , is a crystalline substance melting at  $13.5^\circ$ . *Hexadecylidene*,  $\text{C}_{16}\text{H}_{30}$ , crystallises in hard lustrous tables, melts at  $20^\circ$  and boils at  $160^\circ$  under 15 mm. pressure. Sp. gr. = 0.8039 at  $20^\circ$ , 0.7969 at  $30^\circ$ .

*Octadecylene bromide*,  $\text{C}_{18}\text{H}_{36}\text{Br}_2$ , crystallises in silvery tables, melts at  $24^\circ$ , and is sparingly soluble in alcohol. *Octadecylidene*,  $\text{C}_{18}\text{H}_{34}$ , crystallises in large plates, melts at  $30^\circ$ , and boils at  $184^\circ$  under 15 mm. pressure. Sp. gr. = 0.8016 at  $30^\circ$ .

The physical properties of these members of the acetylene series are compared in the following table:—

		Melting point.	Sp. gr. at the melting point.	Boiling at 15 mm.
Dodecylidene ..	$\text{C}_{12}\text{H}_{22}$	$-9^\circ$	$d_{-9} = 0.8097$	$105^\circ$
Tetradecylidene.	$\text{C}_{14}\text{H}_{26}$	$+6.5^\circ$	$d_{6.5} = 0.8064$	$134^\circ$
Hexadecylidene.	$\text{C}_{16}\text{H}_{30}$	$20^\circ$	$d_{20} = 0.8039$	$160^\circ$
Octadecylidene.	$\text{C}_{18}\text{H}_{34}$	$30^\circ$	$d_{30} = 0.8016$	$184^\circ$

From this table it will be seen that the law put forward by the author as to the density of the normal paraffins and olefines immediately above the point of fusion (*Abstr.*, 1882, 1272; this vol., 572), also holds good for the higher members of the acetylene series.

"Equal volumes of fused acetylenes have (very nearly) equal weights." In all three series a difference in composition of  $C_2H_4$  is equal to a difference of about 35.7 in the molecular volume of the liquid immediately above its fusing point.

A. J. G.

**The so-called Rubeanhydric Acid (Cyanogen Bisulphhydrate).** By R. WOLLNER (*J. pr. Chem.* [2], 29, 129—131).—The author has prepared this compound,  $C_2N_2H_4S_2$ , by passing dry cyanogen gas into an alcoholic solution of sodium sulphydrate; on adding hydrochloric acid, the cyanogen bisulphhydrate is precipitated. If the solution, after treating it with cyanogen, is allowed to stand for some hours, decomposition takes place, and on adding hydrochloric acid no precipitate is obtained. The author considers the free acid to be an imido-derivative,  $[C(NH).SH]_2$ , of the as yet unknown thioxalic acid,  $(CO.SH)_2$ .

J. I. W.

**Action of Iodine on Potassium Seleniocyanate.** By A. VERNEUIL (*Bull. Soc. Chim.* 41, 18—20). Chlorine, bromine, and iodine act on an aqueous solution of potassium seleniocyanate forming red crystalline precipitates. The compounds are not easily isolated unless precautions be taken to avoid excess of the halogen. In studying the action of iodine on potassium seleniocyanate, the author uses a liquid containing 93 parts of iodine and 120 of potassium iodide dissolved in 100 parts of water. 15 c.c. of this liquid suffice to completely react with 10 grains of potassium seleniocyanate dissolved in 100 c.c. of water. As the iodine solution is gradually added, a red crystalline precipitate is thrown down; this is filtered off and the liquid allowed to stand without access of air when more crystals are deposited. The total yield is about 50 per cent. of the potassium seleniocyanate operated on. The crystals dried by pressure or over sulphuric acid contain selenium, cyanogen, potassium, water, and iodine. The latter, which is present to the extent of about 4 per cent., the author regards as an impurity from adhering cyanogen iodide. Leaving this out of consideration, the results lead to the formula  $K(CN)_3Se_4H_2O$ . The other products of the reaction are potassium iodide and cyanogen iodide, both of which remain dissolved in the aqueous liquid. The decomposition is probably expressed by the equation  $4KCNSe + 2I_2 + H_2O = K(CN)_3Se_4H_2O + 3KI + CNI$ . The new compound forms ruby-red crystals having an odour of hydrocyanic acid and hydrogen selenide. The crystals, when treated with water or exposed to moist air, are at once decomposed, producing principally potassium seleniocyanate and free selenium. When heated to  $120^\circ$ , they are decomposed, yielding potassium seleniocyanate, selenium, and cyanogen. The compound is insoluble in ether, chloroform, and carbon bisulphide. Admixture with absolute alcohol causes the deposition of selenium and the formation of a new body which remains in solution, but can be obtained in brown crystals by evaporating the liquid in a vacuum. This compound is potassium per-seleniocyanate,  $K(CN)_3Se_3$ . It is at once decomposed by water, but is dissolved by absolute alcohol. When this compound is heated, it yields potassium seleniocyanate, selenium, and cyanogen.

W. R. D.

**Preparation of Ethereal Salts by Double Decomposition.**

By G. BERTONI and F. TRUFFI (*Gazzetta*, 14, 23—29). Bertoni had previously found (*Gazzetta*, 1882) that when amyl nitrite is digested with ethyl or methyl alcohol double decomposition takes place with formation of ethyl or methyl nitrite and regeneration of amyl alcohol. The authors in this paper give the results obtained with normal propyl alcohol (b. p. 97°) and isobutyl alcohol (b. p. 107°). The amyl nitrite employed was prepared from fermentation amyl alcohol boiling between 128° and 132°.

*Propylic nitrite*.—Amyl nitrite and propyl alcohol in molecular proportions were placed in a flask furnished with a four-bulb fractionating tube, and gradually heated, collecting the portion which came over below 64°; this, after being dried with fused calcium nitrate and submitted to fractional distillation, gave pure propyl nitrite (b. p. 57°), which was subsequently completely reconverted into propyl alcohol by digestion with methyl alcohol. It was found that 51·6 per cent. of the propyl alcohol was converted into the nitrite.

*Isobutyl nitrite*.—On heating a mixture of amyl nitrite and isobutyl alcohol in the manner described above, isobutyl nitrite was obtained boiling at 66—70°, the proportion of the alcohol converted, however, being only 37·8 per cent. in this instance. Several repetitions of these experiments were made, and from the results and those obtained in the former research, he deduces the following:—

*Limit of the Formation of Nitrites by Double Decomposition.*

Methyl alcohol	=	100	per cent.
Ethyl	"	85	"
Propyl	"	52	"
Isobutyl	"	37	"

The limit of etherification decreases with the molecular weight, and moreover this decrease is regular, for if we consider the difficulty of separating the whole of the propyl and isobutyl nitrites formed, it is more than probable that the numbers found are somewhat too low: if we make that for propyl alcohol 55 and for isobutyl alcohol 40, the limits become 100, 85; 55 and 40 per cent. respectively, and the differences  $100 - 85 = 15$ ;  $85 - 55 = 30 = 2 \times 15$ ; and  $55 - 40 = 15$ . The author also draws attention to the fact that the differences between the boiling points A of the alcohols, and of the corresponding nitrites B, is in almost every case 40°.

Alcohol.	Amyl primary normal.	Fermentation amyl.	Butyl primary normal.	Isobutyl.	Normal propyl.	Isopropyl.	Ethyl.	Methyl.
A .....	137°	132°	116°	107°	97°	84·6°	78°	67°
B .....	97	92	76	67	57	44·5	18	13
Difference..	40	40	40	40	40	40·1	60	80

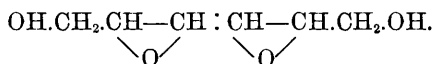
C. E. G.

**Second Anhydride of Mannitol.** By A. FAUCONNIER (*Bull. Soc. Chim.* **41**, 18—20). In addition to the reactions described in a former Abstract (Abstr., 1883, p. 305), the following have been investigated. The body appears to be isomeric with the mannide of Berthelot, and for this reason is called by the author *isomannide*. It is dextrorotatory, a solution in ethyl alcohol is more dextrorotatory than an aqueous solution, and the solution in methyl alcohol has a still greater rotatory action. Gaseous hydrochloric acid does not act on isomannide either in the cold or at 100°, even in presence of zinc chloride, but when an aqueous solution of the substance is saturated with the gas at 0°, and the liquid heated in a sealed tube for some days at 100° *mannitol dichlorhydrin*,  $C_6H_{12}O_4Cl_2$ , is formed. In addition to the diacetyl-derivative previously described, a mono-derivative,  $C_6H_9O_3 \cdot \overline{Ac}O$ , has been produced by the action of acetic chloride: it is a colourless liquid boiling at 185—187° under a pressure of 25 mm., insoluble in water, soluble in ether. When isomannide is heated with methyl iodide and concentrated potash solution, a monomethyl-derivative,  $C_6H_9O_3 \cdot OMe$ , is formed in crystals which melt at 44—45°. A diformic-derivative,  $C_6H_8O_2(CHO_2)_2$ , was obtained by the action of formic acid on isomannide. It forms crystals which melt at 115°, and are very soluble in warm alcohol, slightly in cold water, more so in ether. It is decomposed when distilled under the ordinary pressure, carbonic oxide being evolved and isomannide formed.

From the reactions of isomannide, the author concludes that it is a saturated body the molecule of which contains no doubly linked carbon-atoms. The two alcoholic hydroxyl-groups are not in the vicinity of one another. The other two atoms of oxygen are each united to two different carbon-atoms constituting two  $:C \text{---} C:$  groups.



If it be admitted that the constitution of mannitol is symbolised by a symmetrical open chain, the following formula represents the reactions of isomannide—



This formula however needs further confirmation by a study of the oxidation-products of isomannide of which so far only oxalic acid has been obtained.

W. R. D.

**Action of Cupric Hydroxide on Sugars.** Part II. By J. HABERMANN and M. HONIG (*Monatsh. Chem.*, **5**, 208—216). (See Abstr., 1883, 38).—*Galactose*.—This sugar was prepared according to Soxhlet's method (*J. pr. Chem.* [2], **21**, 269) from milk-sugar; clear proof was obtained that the second sugar formed at the same time was dextrose. In this, as in all other cases of oxidation with cupric hydroxide, the products were the same whether the oxidation was effected in neutral or alkaline solution, the presence of alkali merely accelerating the reaction. The products of the oxidation of galactose are carbonic anhydride, formic acid, a very small quantity of glycollic

acid, a relatively larger quantity of lactic acid, and a non-volatile acid (or mixture of acids) insoluble in ether, whose calcium salt is amorphous and insoluble in alcohol.

With regard to the course of the reaction, the cupric hydroxide begins to be decolorised soon after the commencement of boiling; it had changed to yellowish-green in half an hour and in one hour to nearly pure reddish-yellow. Evolution of carbonic anhydride commences with the beginning of change of colour in the copper oxide, but at first there is not much evolved. With the portions of cupric hydroxide added later reduction is more quickly effected, and carbonic anhydride is copiously evolved.

With *milk-sugar*, the course of the reaction is similar to that observed with *can-sugar*, inversion apparently preceding oxidation. The products are identical with those observed in the case of galactose, but the amount of glycollic acid formed exceeds that of the lactic acid.

With *maltose*, the reduction of the cupric oxide proceeds very quickly. Three stages can be observed in the reaction, the first evidently during inversion, the second and third similar to those seen in the case of grape-sugar. The products both in their qualitative and quantitative relations are identical with those from dextrose.

The oxidation of *Sorbin* occurs more quickly and energetically than that of any other sugar. The products are: 1, Carbonic anhydride in large quantity; 2, Formic acid in relatively large amount; 3, a very small quantity of a brown substance soluble in ether, and consisting of a mixture of an indifferent resinous substance with an acid whose barium salt forms a brown amorphous mass; and 4, an acid of the empirical formula  $C_3H_4O_6$ . This acid may possibly be glyceric acid, but the authors have not yet sufficient evidence to speak positively.

Mannitol and dulcite have no action on cupric hydroxide either in neutral or alkaline solution.

A. J. G.

**Rate of Reduction of Fehling's Solution by Sugars.** By F. URECH (*Ber.*, **17**, 1539—1543).—With a view to determine the composition of invert milk-sugar, the author has experimented on the rate of reduction of Fehling's solution by dextrose, levulose, invert sugar from saccharose, milk-sugar, invert milk-sugar, and various mixtures of the same. He concludes that invert milk-sugar must consist either of dextrose and galactose, or of lactoglucose and galactose. Which of these views is correct must be decided by determining the rate of reduction by galactose and by mixtures of dextrose with galactose.

L. T. T.

**Action of Alkalis on Invert-sugar, Dextrose, and Milk-sugar.** By F. URECH (*Ber.*, **17**, 1543—1547).—The action of alkalis tends to diminish the reducing power of these sugars.

L. T. T.

**Birotation of Glucose and Milk-sugar.** By F. URECH (*Ber.*, **17**, 1547—1549).—The sparing solubility of milk-sugar in water makes the rapid determination of its birotary power difficult. The highest ratio the author has obtained is 1 : 1.62. With glucose at

low temperatures, the author has obtained ratios up to 1 : 2·19. From a comparison of the results obtained with glucose and milk-sugar, he believes the birotation-ratio with milk-sugar would certainly be as much as 1 : 2, if it could be determined correctly. The rotation diminishes from the moment of solution, and the rate of diminution increases with rise of temperature.

L. T. T.

**Inversion of Cane-sugar.** By W. OSTWALD (*J. pr. Chem.* [2], 29, 385—408).—The author has determined the velocity with which cane-sugar is inverted by various acids. The method of experiment was to take 10 c.c. of a solution of sugar (40—50 per cent.), and dilute it with 10 c.c. of a normal acid solution (1 equiv. per litre). The liquid was then heated at 25°, and at the end of each hour the amount of sugar inverted was estimated by the polariscope. The experiments were carried out with 32 acids, and the velocity of the reaction was found to vary with the different acids. The formula representing the progress of the reaction is the same as that found for the action of acids on methyl acetate (this vol., 581):  $\log b - \log (b - x) = a.c.t$ ; where  $a$  represents the amount of the acid and

	I.	II.	III.
Hydrochloric acid .....	100·0	100·0	100·0
Hydrobromic acid .....	111·4	105·5	99·1
Nitric acid .....	100·0	100·0	95·7
Chloric acid .....	103·5	101·8	97·2
Sulphuric acid .....	53·60	73·2	73·9
Ethyl hydrogen sulphate .....	100·00	100·0	99·3
Isethionic acid .....	91·8	95·9	98·9
Ethylsulphonic acid .....	91·2	95·4	98·9
Benzenesulphonic acid .....	104·4	102·2	95·5
Formic acid .....	1·53	12·4	11·5
Acetic acid .....	0·400	6·32	5·87
Isobutyric acid .....	0·335	5·79	5·18
Monochloroacetic acid .....	4·84	22·0	20·8
Dichloroacetic acid .....	27·1	52·1	48·0
Trichloroacetic acid .....	75·4	86·8	82·6
Glycollic acid .....	1·308	11·4	—
Lactic acid .....	1·066	10·3	9·49
Methylglycollic acid .....	1·815	13·5	—
Ethylglycollic acid .....	1·372	11·7	—
Methyl-lactic acid .....	1·390	11·8	—
Diglycollic acid .....	2·67	16·3	—
Pyroacetic acid .....	6·49	25·5	25·9
Glyceric acid .....	1·715	13·1	—
Hydroxybutyric acid .....	1·062	10·3	9·60
Oxalic acid .....	18·57	43·0	43·0
Malonic acid .....	3·18	17·5	16·9
Succinic acid .....	0·545	7·38	7·04
Pyrotartaric acid .....	1·070	10·3	—
Malic acid .....	1·271	11·3	10·9
Citric acid .....	1·725	13·1	12·8
Phosphoric acid .....	6·21	24·9	—
Arsenic acid .....	4·81	21·9	—



is constant,  $b$  the amount of sugar used, and  $x$  the amount of sugar inverted in the time  $t$ . The results found for the constant  $a.c$  are in the case of each acid and each observation very close.

The relation between the constants of inversion and the affinities of the acids is well marked. In the table (p. 1113) is given, in the first column, the value for  $c$  in the case of each acid, referred to  $\text{HCl} = 100$ ; in the second the square root of the number is given referred again to  $\text{HCl} = 100$ ; and for comparison in the third column the square root of the velocity in the decomposition of methyl acetate.

The author also gives a table of the values of  $\log \frac{b}{b-x}$  for all values of  $\frac{x}{b}$  between 0.001 and 0.999 for the use of those who may wish to pursue similar investigations.

A. B.

**Action of Bromine in Alkaline Solution on Amines.** Part V. By A. W. HOFMANN (*Ber.*, 17, 1406—1412).—A continuation of the author's work on this subject (*Abstr.*, 1882, 822, 950, and 1052). In the last paper, the formation of nitriles in this reaction was mentioned, the author being then of opinion that this was due simply to the elimination of water from the amide, but on examination of the nitrile it was found that it contained 1 carbon-atom less than the amide, that is, it corresponded to the amine formed in the reaction, and doubtless is derived from it by the removal of 4 hydrogen-atoms. The reaction was worked out most fully with the amide of nonylic acid; this, on treatment with bromine and alkali, yielded octylamine, octylnonoxycarbamide, and octonitrile, the yield of the latter being from 25—30 per cent. On heating octonitrile with sulphuric acid it is converted into an octylamide (caprylamide), identical with that obtained from caprylic acid, or the acids derived from heracleum oil and from cocoanut oil; the identity of the two acids last named with caprylic acid being thus established. By treatment with alkali and bromine, octylamine can be converted, in part into heptylnitrile, and further by successive conversions into amide and nitrile, the successive amides and nitriles down to normal valeramide were prepared; scarcity of material then prevented the reaction being carried further.

A. J. G.

**Some New Alkines.** By L. BEREND (*Ber.*, 17, 510—512).—*Tetramethylallylalkine*,  $\text{C}_3\text{H}_5(\text{OH})\text{Me}_4\text{N}_2$ , is obtained by heating symmetrical dichlorohydrin with dimethylamine; the product is treated with potassium hydroxide, and then extracted with chloroform. It is a liquid boiling between  $170^\circ$  and  $185^\circ$ . Its platinochloride crystallises in yellow, silvery leaflets, sparingly soluble in water. Its benzoylalkine forms a platinochloride crystallising in orange-red tables, very little soluble in water.

*Tetrethylallylalkine*,  $\text{C}_3\text{H}_5(\text{OH})\text{Et}_4\text{N}_2$ , obtained from diethylamine and symmetrical dichlorohydrin, is a colourless, highly refractive liquid boiling at  $234.5^\circ$ . It has a sp. gr. of 0.9002 ( $\text{H}_2\text{O}$  at  $4^\circ = 1$ ), and is identical with that obtained by Reboul (*Abstr.*, 1884, 578) from

epichlorhydrin. Its platinochloride crystallises in prisms, soluble in water. The platinochloride of the benzoylalkaine is obtained as an orange-coloured powder.

The *tetretethylallylalkaine* obtained from unsymmetrical dichlorhydrin is a liquid; its aurochloride crystallises in leaflets, and is sparingly soluble in water. Its benzoyl-derivative forms a platinochloride crystallising in orange-red needles, and is more soluble in water than its isomeride.

*Trimethylenediethylalkaine*,  $C_7H_{17}NO$ , obtained from trimethylenechlorhydrin and dimethylamine, is a colourless, strongly refractive liquid, having a sp. gr. 0.9199 at  $4^\circ$  and boiling at  $189.5^\circ$ . The author has prepared its platino- and auro-chlorides, also the platinochloride of the benzoylalkaine.

P. P. B.

**Acetoximes of the Fatty Series.** By E. SPIEGLER (*Monatsh. Chem.*, **5**, 241—243; and *Ber.*, **17**, 1574).—These experiments were made to ascertain if ketones of high molecular weight behaved with hydroxylamine in a manner similar to those of low molecular weight. The result showed the nature of the reaction to be identical, although as was to be expected it proceeded more slowly. The ketones were dissolved in alcohol, mixed with an excess of hydroxylamine, and heated for some days on the water-bath.

*Methylnonylacetoxime*,  $C_{11}H_{23}NO = C_9H_{19}.CMe:NOH$ , prepared as above from methyl nonyl ketone, forms snow-white minute prisms or long slender needles, and melts at  $42^\circ$ .

*Myristoxime*,  $C_{27}H_{55}NO = C(C_{13}H_{27})_2NOH$ , prepared from myristone (dimyristyl ketone), is a white amorphous substance melting at  $51^\circ$ .

*Stearoxime*,  $C_{35}H_{71}NO = C(C_{17}H_{35})_2NOH$ , prepared from stearone (distearyl ketone), forms an amorphous substance similar in appearance to stearin, and melts at  $62-63^\circ$ .

A. J. G.

**Optical Rotatory Power of Leucine.** By J. LEWKOWITSCH (*Ber.*, **17**, 1439—1440).—The author has found leucine in aqueous solution to be laevorotary, whilst in a recent paper Mauthner (*Zeits. Physiol. Chem.*, **7**, 22) states that leucine from casein is dextrorotary. In a private communication, Mauthner has since admitted that leucine is laevorotary in aqueous solution, whilst in acid or alkaline solution, on the contrary, it is dextrorotary.

A. J. G.

**Derivatives of Succinimide.** By G. L. CIAMICIAN and P. SILBER (*Gazzetta*, **14**, 31—38; and *Ber.*, **17**, 553—559).—*Dichloromaleimide* may be prepared by acting on succinimide with chlorine (*Gazzetta*, **13**, 413, and this vol., 292), but not more than 25 grains of the imide should be employed in each operation; the yield is 52 per cent. of the theoretical. When an alcoholic solution of dichloromaleimide is allowed to evaporate spontaneously it is deposited in well-defined crystals belonging to the trimetric system; these have been measured by La Valle with the following results:—

$$a : b : c = 0.99224 : 1 : 1.59336.$$

Observed forms 001, 010, 100, 334, 111. Combinations the same. Cleavage easy, parallel to 001.

When dichloromaleimide is heated with phosphorus pentachloride for 24 hours at 200°, and the liquid product poured into water and distilled in a current of steam, a compound,  $C_4Cl_7N$ , passes over along with some unaltered dichloromaleimide, whilst resinous matters, dichloromaleimide and dichloromaleic acid, remain in the retort. In order to separate the new substance from the imide which accompanies it, the oil is separated from the aqueous portion of the distillate and boiled two or three times with fresh quantities of water, using a reflux condenser; in this way most of the imide is dissolved out, and after a final distillation in a current of steam, the oil is allowed to solidify over sulphuric acid, pressed between paper and distilled under diminished pressure. It then forms a white opaline waxy mass, which melts at 70—73°, and distils without decomposition at 143—144° under a pressure of 20 mm., and at 261° at 754 mm. with partial decomposition. It is exceedingly soluble in alcohol, ether, and glacial acetic acid, but almost insoluble in boiling water. It is converted into tetrachloropyrroline,  $C_4Cl_4NH$ , by the action of zinc and hydrochloric acid. The authors assign to the new chloride

$C_4H_7N$  the constitution  $\left| \begin{array}{l} CCl_2.CCl_2 \\ CCl_2.CCl \end{array} \right\rangle N$ , and remark that it closely re-

sembles the perchloride of perchloropyrroline (this vol., 292) both in chemical and in physical properties. The authors endeavoured to displace the chlorine in tetrachloropyrroline by hydrogen, but the results were not very satisfactory; sodium amalgam and acetic acid had no action, neither was any change produced by boiling it with zinc-dust and potash solution, unless the latter was very concentrated, and the action very prolonged; under these circumstances, however, an oil was obtained on distilling the product with steam, but of so unstable a character that it could not be distilled alone. When the compound  $C_4Cl_7N$  is heated with hydriodic acid and phosphorus, it is converted into a reddish-brown resinous matter, probably "pyrrol-red."

*Dibromomaleimide*,  $C_4Br_2O_2 : NH$ .—By acting on succinimide with bromine, Kisielinski obtained monobromofumarimide, and a compound melting at 225° which he regarded as dibromosuccinimide. The authors have repeated Kisielinski's experiments, and find that the substance melting at 225° is really dibromomaleimide, as might be expected from the results obtained by the action of chlorine on succinimide. The most convenient way of preparing it is to allow bromine (25 grams) to drop slowly on the succinimide (10 grams) heated at about 160° in a retort; hydrobromic acid is evolved, and the residue, after being pulverised, is washed with water to remove monobromofumarimide, and crystallised two or three times from boiling alcohol with the aid of animal charcoal. It then yields the dibromomaleimide in a state of purity: this is insoluble in water, but easily in ether and in boiling alcohol. Well developed crystals belonging to the monoclinic system are obtained by allowing an alcoholic, or still better an acetone solution of the substance to evapo-

rate spontaneously. These have been measured by La Valle, who finds:—

$$a : b : c = 1.434208 : 1 : 0.964913 \\ = 119.59^\circ$$

Observed forms, 100, 101, 110,  $\bar{1}11$ .

Combinations, 100, 001, 110,  $\bar{1}11$ ; 100, 110,  $\bar{1}11$ .

Cleavage perfect and easy parallel to 001.

Plane of the optic axes 010.

The dibromomaleïmide, when boiled with potash until ammonia ceases to be evolved, is decomposed with formation of *dibromomaleïc acid*,  $C_4Br_2O_3$ , which may be isolated by acidifying the aqueous solution with sulphuric acid and extracting with ether. It melts at  $123-125^\circ$ , and has all the properties of the acid obtained from succinic acid by Kekule, and from pyromucic acid by Hill. When distilled in a current of carbonic anhydride, it yields the corresponding anhydride; this melts at  $114-115^\circ$ , and is reconverted into the acid by boiling with water. The *barium salt*,  $C_4Br_2BaO_4 \cdot 2H_2O$ , and the *silver salt* were prepared.

C. E. G.

#### Action of Zinc Propyl and Zinc Isobutyl on Butyl Chloral.

By K. GARZAROLLI-THURNLACKH and A. POPPER (*Annalen*, **223**, 166—169).—Trichlorobutyl alcohol and propylene are formed by the action of zinc propyl on butyl chloral.

Trichlorobutyl alcohol is also formed when butyl chloral is acted on by zinc isobutyl. Zinc propyl and isobutyl resemble zinc ethyl in their action on butyl chloral. Zinc isobutyl boils at  $166^\circ$ , not at  $186^\circ$  as stated by Cahours.

W. C. W.

**Preparation of Chloral.** (*Dingl. polyt. J.*, **252**, 343).—According to Page, a larger yield is obtained when the alcohol used for the preparation of chloral is treated with 5 per cent. ferric chloride or thallium chloride previous to the introduction of chlorine. The resulting liquid, consisting of a mixture of chloral, hydrate of chloral, and chlorinated ethanes, which can be separated by fractional distillation, is subjected to distillation, ferric chloride or thallium chloride remaining in the residue. The chlorinated ethanes which come over at a temperature above  $100^\circ$  are purified by fractional distillation, the mixture of chloral and hydrate of chloral is distilled over calcium carbonate, treated with the requisite quantity of water, and the resulting hydrate of chloral recrystallised from the chlorinated ethanes previously obtained.

D. B.

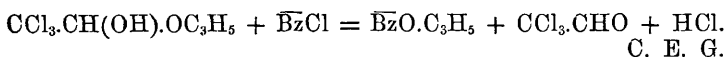
**Action of Acid Chlorides on Chloral Allylate.** By V. OLIVERI (*Gazzetta*, **14**, 13—14).—Ogliolero (*ibid.*, **4**, 463) regards chloral allylate—prepared by the action of allyl alcohol on chloral—as containing alcoholic hydroxyl, its constitution being expressed by the formula  $CCl_3 \cdot CH(OH) \cdot O \cdot CH_2 \cdot CH : CH_2$ ; other chloral alcoholates having analogous formulæ. In order to obtain evidence on this subject, the author submitted the allylate to the action of acetic and benzoic chlorides.

Acetic chloride acts on chloral allylate in the cold, but it is neces-

sary to heat the mixture for a short time at  $100^{\circ}$  in order to complete the reaction. The product, after being washed with water, dried over calcium chloride, and purified by fractional distillation, is a colourless, oily, highly refractive liquid, which boils at  $105^{\circ}$  to  $107^{\circ}$ . The results of the analysis correspond with the formula



The action of benzoic chloride is less energetic, and it is necessary to heat the mixture; the product is shaken with sodium carbonate solution to remove benzoic acid, rapidly separated, washed with water, dried, and distilled. The distillate is an oily liquid boiling at  $225$ — $227^{\circ}$ , and has all the properties of allyl benzoate. In the case of benzoic chloride, therefore, it would seem that the reaction is



**Action of Zinc Ethyl and Zinc Methyl on Chlorinated Aldehydes.** Part III. By K. GARZAROLLI-THURNLACKH (*Annalen*, **223**, 149—165).—*Methyl trichloropropyl carbinol*,  $\text{C}_5\text{H}_9\text{Cl}_3\text{O} = \text{CHMeCl}\cdot\text{CCl}_2\cdot\text{CHMe}\cdot\text{OH}$ , prepared by the action of zinc methyl on butyl chloral diluted with ether, crystallises in silky needles which melt at  $50\cdot5^{\circ}$ , and under a pressure of 41 mm., boils at  $123^{\circ}$ . It is soluble in alcohol and ether.

The *acetate* is a colourless liquid boiling at  $227^{\circ}$ . Its sp. gr. at  $11\cdot5$  is  $1\cdot3048$ . The alcohol is oxidised by treatment with nitric acid, yielding carbonic anhydride and trichlorobutyric acid. On oxidation with chromic mixture, methyl trichloropropyl ketone boiling at  $192^{\circ}$  is formed. On further oxidation, the ketone splits up into acetic and hydrochloric acids and carbonic anhydride.

If the alcohol is treated with zinc and hydrochloric acid, or with iron powder and acetic acid, it is converted into methyl monochlorallyl carbinol,  $\text{C}_5\text{H}_9\text{ClO} = \text{CHMe}:\text{CCl}\cdot\text{CHMe}\cdot\text{OH}$ ; this is a colourless liquid boiling at  $158^{\circ}$ , sp. gr.  $1\cdot08821$  at  $14\cdot1^{\circ}$ . It yields acetic acid and carbonic anhydride on oxidation. The acetate boils at  $172^{\circ}$  and the chloride at  $143^{\circ}$ . The chloride unites with bromine, forming *methyl-monochlorodibromopropyl-carbinyl chloride*, a heavy liquid boiling between  $140^{\circ}$  and  $145^{\circ}$  under 31 mm. pressure.

W. C. W.

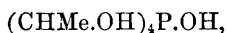
**Occurrence of Valerolactone in Pyroligneous Acid.** By M. GRODZKI (*Ber.*, **17**, 1369).—The author has isolated from the higher boiling fractions of crude pyroligneous acid a substance agreeing in all respects with the description of valerolactone given by Fittig and Messerschmidt (*Abstr.*, 1882, 35).

A. J. G.

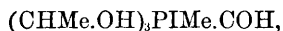
**Phosphine-derivatives of the Aldehydes.** By A. DE GIRARD (*Ann. Chim. Phys.* [6], **2**, 1—66).—The close analogy between the hydrogen-derivatives of nitrogen and phosphorus, rendered closer by the recent discovery of phosphonium chloride and hydroxyl, points to the possible isolation of organic derivatives of phosphorus hitherto unknown.

With a view of preparing phosphorus analogues of the aldehyde-ammonias, the author has particularly studied the action of phosphonium iodide on the aldehydes. The products of the reaction are combinations of 4 mols. of the aldehyde with 1 mol. of phosphonium iodide, of which those of ethylic, propionic, valeric, and cœnanthylic aldehydes are well-defined crystalline substances. These are designated by the names of *tetrahydroxyethylidene-, propylidene-, amylidene-, and cœnanthylidene-phosphonium iodides*.

*Tetrahydroxyethylidene-phosphonium iodide*,  $(\text{CHMe.OH})_4\text{PI}$ , obtained from parethaldehyde and phosphonium iodide, crystallises in white prisms, which gradually lose hydriodic acid. It is soluble in water and alcohol, insoluble in ether and chloroform. Its solutions give a maroon-coloured precipitate with copper sulphate, and a yellow precipitate with silver nitrate. It is converted by a concentrated solution of potash into the corresponding hydroxyl-derivative,



crystallising in rhombohedric laminæ; this readily loses a molecule of water, being converted into a substance of the composition



an oily liquid, which on evaporation forms a confusedly crystalline mass. The liquid is soluble in water and alcohol, sparingly soluble in ether. It readily reduces potassium permanganate and solutions of silver salts, with formation of silver phosphate and acetate.

The corresponding derivatives of propaldehyde resemble those of ethaldehyde in their chemical and physical properties.

*Tetrahydroxamylidene-phosphonium iodide*,  $(\text{C}_5\text{H}_{10}\text{.OH})_4\text{PI}$ , prepared from phosphonium iodide and valeraldehyde, crystallises in rhombohedric laminæ melting at  $119^\circ$ . It is converted by potash into the corresponding hydroxyl-derivative of the formula  $(\text{C}_5\text{H}_{10}\text{O})_3\text{PH}_4\text{.OH}$ , which crystallises in white prisms melting at  $125-126^\circ$ , insoluble in water. The derivatives of cœnanthaldehyde resemble those of valeraldehyde. Similarly chloral hydrate forms *dihydroxy-chloral-phosphine*,  $(\text{CCl}_3\text{.CHO})_2\text{PH}_3$ , crystallising in small hard prisms, which melt at  $143^\circ$ . It is soluble in water and alcohol. It reduces salts of silver, and is decomposed by potash into hydrogen, hydrochloric, formic, and hypophosphorous acids. The corresponding butyl-derivative,  $\text{C}_4\text{Cl}_3\text{H}_5\text{O.PH}_3$ , crystallises in white prisms, which melt at  $96^\circ$ . It is soluble in alcohol and ether, and readily reduces salts of silver.

The products of the reaction of phosphonium iodide on isobutylic, benzoic, and salicylic aldehydes and acetone were also examined, but were not obtained in a sufficiently definite form. V. H. V.

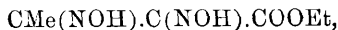
**Vapour-density of Tertiary Amyl Compounds.** By N. MENSCHUTKIN and D. KONOWALOFF (*Ber.*, 17, 1361—1364).—In some experiments made by the authors on the decomposition and dissociation of the tertiary amyl compounds by heat, it was found that the nature of the substances in contact with the liquid or vapour exercised a very great influence on its dissociation. It was found, for

instance, that amyl acetate gave the normal vapour-density in Hofmann's apparatus at 158°, whilst at the same temperature in a Victor Meyer's air-displacing apparatus, on the bottom of which was placed some asbestos to break the fall of the bottle containing the substance, the density was but little above half the normal, whilst on replacing the asbestos by mercury, or by using an empty apparatus, numbers only slightly below the normal were obtained. It was found that bottles with ground glass stoppers exerted a similar decomposing influence; even the difference in the amount of ground surface in two bottles having different sized stoppers caused a most marked difference in the vapour-densities determined by their aid under conditions otherwise identical. A. J. G.

**Methyl-propyl-acetic Acid.** By C. LIEBERMANN and S. KLEEMANN (*Ber.*, 17, 918—921).—The methyl-propyl-acetic acid from saccharose (Abstr., 1883, 1078), although believed to be identical with Saytzeff's methyl-propyl-acetic acid (*ibid.*, 408), shows some points of difference. To confirm the identity, methyl-normal-propyl-acetic acid was prepared. Ethylic methyl-acetoacetate is heated with normal propyl iodide and sodium alcoholate, and on removing the alcohol and adding water an oil separates, boiling at 214°. This is the *ethylic* salt of methyl-normal-propyl-acetoacetic acid; its sp. gr. is 0.9585 at 15°. When heated with alkalis, it yields methyl-normal-propyl-acetic acid, an oily liquid boiling at 193—194°, and having a sp. gr. of 0.9217 at 25° (the acid from saccharose 0.9231, Saytzeff's 0.9227). Neither the free acid nor its derivatives act on polarised light, although they contain an asymmetrical carbon-atom. The lead salt is a heavy oil; only twice was it obtained crystalline, once in the form described by Saytzeff, and once as described by Liebermann and Scheibler (Abstr., 1883, 1078); the crystals melt at 43°. The zinc salt melts at 72°, as described by Kelbe and Warth, who prepared their acid from resin oil (vol. 42, 711), and the calcium salt has also the properties mentioned by them.

Methyl-normal-propyl-acetic acid is therefore identical with the acids previously prepared by Liebermann and Schiebler, by Saytzeff, and by Kelbe and Warth. H. B.

**$\alpha$ - $\beta$ -Diisonitrosobutyric Acid.** By M. CERESOLE and G. KOECKERT (*Ber.*, 17, 819—825).—The action of reducing agents on the various isonitroso-compounds may be classified as follows:—(1.) All isonitroso-compounds that are reduced to amides are acids, and the isonitroso-group stands in the  $\alpha$ -position to the carboxyl-group. It is also possible that bodies containing isonitroso- and hydroxyl-groups attached to adjacent carbon-atoms undergo reduction in a similar manner. (2.) Those isonitroso-compounds which yield a ketine on reduction contain the isonitroso-group attached to a carbon-atom, that is, united to a ketone-carbonyl-group. (3.) Those isonitroso-compounds which do not contain carboxyl- or carbonyl-groups, or do not contain them in the  $\alpha$ -position to the isonitroso-group are incapable of easy reduction.  $\alpha$ - $\beta$ -diisonitrobutyric acid is



and according to the above rules but one of its isonitroso-groups should be capable of reduction. The authors have made experiments to prove this, and communicate the results obtained thus far.

*Ethyl  $\alpha$ - $\beta$ -diisonitrosobutyrate* is prepared by the action of hydroxylamine on an aqueous or alcoholic solution of ethyl isonitroso-acetoacetate. It melts at  $140^\circ$  with decomposition, and may be crystallised from water or ether, &c. By saponification with soda and treatment with sulphuric acid,  *$\alpha$ - $\beta$ -diisonitrosobutyric acid* is obtained; it is crystalline. The barium salt,  $[\text{CMe}(\text{NOH}).\text{C}(\text{NOH}).\text{COO}]_2\text{Ba} + 2\frac{1}{2}\text{H}_2\text{O}$ , is soluble in water, whilst the silver salt,  $\text{C}_2\text{Me}(\text{NOH})_2.\text{COOAg}$ , is almost insoluble.

During the action of hydroxylamine on ethyl isonitrosoacetoacetate, another body is also formed. It is soluble in ether, but having a strongly acid reaction is dissolved by shaking with barium carbonate and water. It may be isolated by acidifying and extracting with ether. It is colourless, melts with decomposition at  $132$ – $133^\circ$ , and is an *external anhydride of  $\alpha$ - $\beta$ -diisonitrosobutyric acid*,  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_7$ . The barium salt,  $\text{BaC}_8\text{H}_8\text{N}_4\text{O}_7 + \frac{1}{2}\text{H}_2\text{O}$ , is deep red in colour, and soluble in water and alcohol. The silver salt forms a red-brown precipitate,  $\text{C}_8\text{H}_8\text{N}_4\text{O}_7\text{Ag}_2$ , insoluble in water. Hence it follows that this anhydride is a dibasic acid, and the union of the two molecules must have taken place through two of the isonitroso-groups. Three constitutional formulæ are possible.

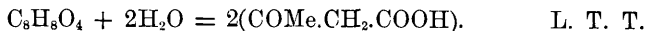
H. B.

**Dehydracetic Acid.** By W. H. PERKIN, jun., and C. BERNHART (*Ber.*, 17, 1522–1527).—When hydroxylamine in excess acts on a concentrated solution of potassium dehydracetate, dehydracetoxime,  $\text{C}_7\text{H}_5\text{O}_3:\text{CNOH}$ , is formed. It is a colourless crystalline substance, soluble in alcohol; and this solution gives an intense purple coloration with ferric chloride. With phenylhydrazine, dehydracetic acid yields *dehydracetophenylhydrazine*,  $\text{C}_8\text{H}_5\text{O}_3\text{N.NHPh}$ , which crystallises in lustrous yellow tables, softening at  $200^\circ$ , and melting with decomposition at  $207^\circ$ . It is soluble in alkaline carbonates, and is reprecipitated by acids. A small quantity of a second compound was also obtained, which melts at  $160^\circ$ , but has not yet been investigated. Monobromodehydracetic acid was obtained by dissolving the acid in chloroform, adding a little iodine and then excess of bromine, and heating for half an hour at about  $50$ – $60^\circ$ . It is thus prepared in a purer state than by Oppenheim and Precht's method (this Journal, 1876, ii, 506). It forms colourless prisms melting at  $136$ – $137^\circ$ . When allowed to remain for 14 days at  $35$ – $40^\circ$  with excess of alcoholic potash, it yields *hydroxydehydracetic acid*,  $\text{C}_6\text{H}_7\text{O}_4.\text{OH}$ . This forms a colourless microcrystalline mass melting at  $250$ – $255^\circ$  with total decomposition. Ferric chloride gives an intense reddish-violet coloration. It is readily soluble in ammonia, and gives a pale-yellow amorphous silver salt of the formula  $\text{C}_6\text{H}_5\text{O}_3\text{Ag}_2$ . Hydroxydehydracetic acid therefore seems to be bibasic. When heated with acetic anhydride, it yields an *acetate* which is crystalline, and melts at  $165$ – $167^\circ$ . With ferric chloride it gives a pale-yellow coloration.

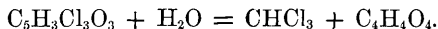
By very careful treatment with *cold* moderately concentrated potash, the authors succeeded in obtaining a small quantity of a



thick oil easily soluble in water. When distilled with steam, this yielded acetone, and was probably acetoacetic acid, which had been formed according to the equation—



**Trichlorophenomalonic Acid. The Constitution of Benzene.** By A. KEKULÉ and O. STRECKER (*Annalen*, 223, 170—197).—In a research on the action of sulphuric acid and potassium chlorate on benzene (*Annalen*, 140, 317; 142, 129; 143, 315; 149, 257; and 155, 217), Carius discovered *trichlorophenomalonic acid*, an unstable compound which is decomposed by warm baryta-water, yielding phenaconic acid. Carius afterwards stated (*Ber.*, 4, 928) that phenaconic acid and fumaric acid are identical. Krafft (*Ber.*, 10, 797) repeated these experiments, and arrived at the conclusion that trichlorophenomalonic acid was nothing else than trichloroquinol. The authors, however, find that trichlorophenomalonic acid is obtained when the directions given by Carius are closely followed, as a slight variation in the process has a great influence on the results. For instance, if the flask containing the mixture of potassium chlorate, sulphuric acid, and benzene is briskly agitated so as to thoroughly mix its contents instead of merely keeping the liquid in a state of rotation, trichloroquinol is produced instead of trichlorophenomalonic acid. Trichlorophenomalonic or  $\beta$ -trichloracetoacrylic acid,  $\text{CCl}_3.\text{CO}.\text{CH}:\text{CH}.\text{COOH}$ , agrees in its properties with the acid described by Carius, but differs from it in composition. It is decomposed by warm baryta-water, with the formation of chloroform and *maleic* not fumaric acid,



Trichlorophenomalonic acid unites with bromine, forming the compound  $\text{C}_6\text{H}_3\text{Cl}_3\text{Br}_2\text{O}_3$ , which crystallises in the triclinic system. It is soluble in alcohol, ether, and chloroform, and melts at  $97.5^\circ$ . On boiling it with milk of lime, (inactive) calcium tartrate is formed.

Trichlorophenomalonic acid is also formed by the action of sulphuric acid and potassium chlorate on quinone. If monochloroquinone is represented by the formula  $\text{C}_6\text{H}_3\text{ClO}_2$  ( $\text{O}:\text{Cl}:\text{O} = 1:4:5$ ), the formation of trichlorophenomalonic acid,  $\text{CCl}_3.\text{CO}.\text{CH}:\text{CH}.\text{COOH}$ , can easily be represented by the following equation:— $\text{C}_6\text{H}_3\text{ClO}_2 + 2\text{HClO}_2 = \text{C}_6\text{H}_3\text{Cl}_3\text{O}_3 + \text{H}_2\text{CO}_3$ , as  $\text{CCl}.\text{CO}.\text{CH}:\text{CH}.\text{CO}$  is common to both the formulæ. As this reaction can be much more easily explained by means of the “ring” than by the “prism” formula for benzene, the authors regard this as further evidence in support of Kekulé’s hypothesis of the constitution of benzene. W. C. W.

**Normal Hydroxyvaleric Acid.** By A. MENOZZI (*Gazzetta*, 14, 16—19).—The acid was prepared from butaldehyde by first heating it with the necessary quantity of hydrocyanic acid of 40 per cent. in sealed tubes; the reaction takes place with slight development of heat, and is completed by heating the mixture first at  $50$ — $60^\circ$  and finally at  $100^\circ$ . The product, which is the nitrile of normal hydroxyvaleric acid, is

saponified by the cautious addition of hydrochloric acid, and the action completed by diluting with water and boiling the mixture for two hours; the hydroxy-acid is then extracted by shaking the solution with ether. In order to purify the crude acid, it is neutralised with potash or soda, and the hot solution precipitated with zinc sulphate, when *zinc hydroxyvalerate*,  $(C_5H_9O_3)_2Zn \cdot 2H_2O$ , is deposited in an amorphous form, but becomes crystalline after a time; the zinc salt is but sparingly soluble even in boiling water, and is deposited from the solution as it cools in long lustrous needles which lose their water of crystallisation at  $100^\circ$ . The free acid may be obtained by decomposing the zinc salt with hydrogen sulphide, and concentrating the solution at first at a gentle heat, and then in a vacuum over sulphuric acid, when it solidifies to a crystalline mass consisting of thin transparent plates; these melt at  $31^\circ$  and sublime at about  $70^\circ$ .

The *calcium salt*,  $(C_5H_9O_3)_2Ca$ , obtained by neutralising the acid with calcium carbonate, crystallises in tufts of small needles which are moderately soluble in water, less so in alcohol. The *cadmium salt*,  $(C_5H_9O_3)_2Cd$ , obtained by treating cadmium carbonate with the acid or by precipitation, is nearly as insoluble as the zinc salt. The *silver salt* is easily soluble in hot water, sparingly in cold, and crystallises in lustrous, colourless prisms. The *ethyl salt* obtained by the action of ethyl iodide on the silver salt is a limpid liquid of agreeable odour, and boils at  $190^\circ$ . C. E. G.

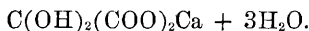
**A New Method of Formation of Pyrotartaric Acid.** F. BEILSTEIN and E. WIEGAND (*Ber.*, **17**, 840—842).—Lactic acid and pyrotartaric acid stand to each other as secondary alcohol and ketone— $CHMe(OH).COOH$  and  $COMe.COOH$ . By the action of bromine, lactic acid is converted into tribromopyrotartaric acid, and it is now shown that lactate of lime treated in dilute solution with potassium permanganate is converted into calcium pyrotartarate—the free acid was isolated, and the barium salt analysed. A new reaction for pyrotartaric acid is that when heated with ammoniacal silver solution it is oxidised with formation of a mirror, with silver oxide it is converted almost quantitatively into silver acetate and carbonic anhydride. Pyrotartaric acid heated with dilute sulphuric acid at  $150^\circ$  is converted into acetaldehyde and formic acid, lactic acid yields acetaldehyde and carbonic anhydride. Probably, this last reaction may explain the ease with which pyrotartaric acid undergoes polymerisation.

H. B.

**Malonic and Tartronic Acids.** By M. FREUND (*Ber.*, **17**, 780—786).—The author refers to a previous paper (this vol., p. 728).

*Potassium ethylmalonate*,  $COOEt.CH_2.COOK$ , cannot be prepared by Van't Hoff's method, but by proceeding in the manner described by the author it can be obtained quite pure. Bromine acts on an aqueous solution of this salt in the same manner as on malonic acid itself, carbonic anhydride and an ethereal salt of brominated acetic acid being formed. By the slow addition of bromine to an acetic acid solution of malonanilide, a white crystalline substance is formed which is *symmetrical malontribromanilide*,  $CH_2(CO.NH.C_6H_4Br_3)_2$ ; it melts at  $145$ — $146^\circ$ , and when heated with nitric acid at  $200^\circ$  yields symmetrical tribrom-

aniline. Using an aqueous solution of malonamide and the calculated amount of bromine, *dibromomalonamide*,  $\text{CBr}_2(\text{CONH}_2)_2$ , separates as a heavy white powder; it is scarcely soluble in cold water or alcohol. By boiling it with silver oxide and water, it is not converted into mesoxalamide, but into ammonium mesoxalate; milk of lime cannot be used instead of silver oxide, and caustic potash gives but a very poor yield. On adding calcium chloride to the aqueous solution a crystalline precipitate of *hydrated calcium mesoxalate* falls,

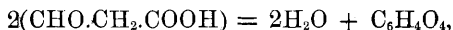


If mercuric oxide be used in place of silver oxide, the compound  $\text{C}_3\text{N}_2\text{H}_2\text{O}_2\text{Br}_2\text{Hg}$  is formed; this is a heavy white powder quite insoluble in alcohol and water. When dimethylmalonamide is treated with bromine in aqueous solution, it also yields a dibromide,  $\text{CBr}_2(\text{CO.NHMe})_2$ , *dibromodimethylmalonamide*, crystallising well and melting at  $162^\circ$ .

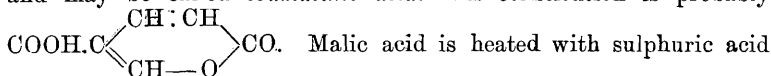
Conrad and Bischoff, by acting on ethyl malonate with chlorine, and on the ethyl monochloromalonate with potash, prepared the potassium and from that the calcium salt of tartronic acid. By acting on this salt with absolute alcohol and hydrochloric acid gas, the author has prepared *ethyl tartronate*,  $\text{CH}(\text{COOEt})_2\text{OH}$ , a liquid boiling at  $218\text{--}219^\circ$  and soluble in ether. When shaken with aqueous ammonia, *tartronamide*,  $\text{CH}(\text{CONH}_2)_2\text{OH}$ , is formed and crystallises out; it melts at  $198^\circ$ .

H. B.

**A Condensation-product of Malic Acid.** By H. v. PECHMANN (*Ber.*, **17**, 936—938).—In the Abstract (p. 1174) reference is made to a condensation-product of the half-aldehyde of malonic acid. Experiments made to isolate this aldehyde failed, but the condensation-product referred to was obtained. It is formed thus:



and may be called *coumalinic acid*. Its constitution is probably



Malic acid is heated with sulphuric acid or zinc chloride until the evolution of gas has ceased, and on adding water to the product the new acid separates for the most part. It is isomeric with an acid recently prepared by Ost. It forms prisms melting at  $205\text{--}207^\circ$  with decomposition, and only sparingly soluble in cold water; when treated with alkalis it is converted into an acid with absorption of water, if warmed a body smelling like crotonaldehyde is obtained and finally fumaric acid. *Methyl coumalinate*,  $\text{C}_6\text{H}_3\text{O}_2.\text{COOMe}$ , crystallises from ether, melts at  $74^\circ$ , and boils at about  $260^\circ$ ; its vapour-density is normal, and it volatilises with steam.

H. B.

**Salts of Mesotartaric Acid.** By S. PRZYBYTEK (*Ber.*, **17**, 1412—1415).—Some doubt having been thrown on the identity of mesotartaric acid and the acid  $\text{C}_4\text{H}_6\text{O}_6$ , prepared by the author from erythrol,

it being in particular stated that the salts of the two acids differ, the author has carefully examined both the acids and their salts, and completely confirms his first statement as to the identity of the two acids.

Calcium mesotartrate,  $C_4H_4CaO_6 + 3H_2O$ , forms characteristic lance-shaped crystals. It is somewhat soluble in glacial acetic acid, 100 parts of acid dissolving 0.028 part of the salt at  $18^\circ$ , and 0.085 at  $100^\circ$ . Hydrogen potassium mesotartrate,  $C_4H_5KO_6$ , can be obtained in needles or lance-shaped crystals by evaporating the aqueous solution very slowly and gradually precipitating by addition of alcohol. The descriptions given of the other salts agree with those already published.

Unsuccessful attempts were made to convert the inactive acid into dextro- and lævo-rotary modifications. A. J. G.

**Constitution of Fatty Acids.** By C. SCHMIDT and A. COBENZL (*Ber.*, **17**, 599—603).—With a view of obtaining an insight into the constitution of the fatty acids, the authors propose to submit to careful investigation the dry distillation of their different salts. Potassium hydrogen mucate and normal potassium mucate have already been investigated; the former yields pyromucic acid, whilst the latter yields dehydromucic acid. P. P. B.

**Higher Homologues of Acetic Chloride.** By F. KRAFFT and J. BÜRGER (*Ber.*, **17**, 1378—1380).—These compounds were prepared from the corresponding pure fatty acids by heating equal molecular weights of the acid and of phosphorous pentachloride in the water-bath; the phosphorous oxychloride formed was removed by heating at  $150^\circ$  under 15 mm. pressure, when the acid chloride was left in a nearly pure state.

*Lauryl chloride*,  $C_{12}H_{23}OCl$ , is a colourless liquid distilling at  $142.5^\circ$  under 15 mm. pressure; it solidifies to a crystalline mass when cooled with liquid sulphurous anhydride, and again melts at  $-17^\circ$ . It has the characteristic odour of the acid chlorides, and is readily decomposed on exposure to moist air. By heating it with phenol and paracresol respectively, it yield *phenyl laurate*,  $C_{18}H_{28}O_2$ , crystallising from alcohol in nacreous plates, melting at  $24.5^\circ$ , and boiling at  $210^\circ$  under 15 mm. pressure, and *paracresyl laurate*,  $C_{19}H_{30}O_2$ , of similar appearance, but melting at  $28^\circ$ , and boiling at  $219.5^\circ$  under 15 mm. pressure.

*Myristyl chloride*,  $C_{15}H_{27}OCl$ , is a colourless liquid; after solidification in a freezing mixture, it melts at  $-1^\circ$ . It boils at  $168^\circ$  under 15 mm. pressure, without essential alteration. *Phenyl myristate*,  $C_{20}H_{32}O_2$ , melts at  $36^\circ$ , and boils at  $230^\circ$  under 15 mm. pressure. *Paracresyl myristate*,  $C_{21}H_{34}O_2$ , melts at  $39^\circ$ , and boils at  $239.5^\circ$  under 15 mm. pressure.

*Palmityl chloride*,  $C_{16}H_{31}OCl$ , melts at  $12^\circ$ , and boils, with slight decomposition, at  $192.5^\circ$  under 15 mm. pressure. *Phenyl palmitate*,  $C_{22}H_{36}O_2$ , melts at  $45^\circ$ , and boils at  $249.5^\circ$  under 15 mm. pressure. *Paracresyl palmitate* melts at  $47^\circ$ , and boils at  $258^\circ$  under 15 mm. pressure.

*Stearyl chloride*,  $C_{18}H_{35}OCl$ , forms a lustrous white crystalline mass, which melts at  $23^\circ$ . Under 15 mm. pressure, it commences to distil at  $215^\circ$ , but marked decomposition ensues on carrying the distillation further. *Phenyl stearate*,  $C_{24}H_{40}O_2$ , melts at  $52^\circ$ , and boils at  $267^\circ$  and 15 mm. pressure. *Paracresyl stearate*,  $C_{25}H_{42}O_2$ , melts at  $54^\circ$ , and boils at  $276^\circ$  and 15 mm. pressure. A. J. G.

**Trichloromethylsulphonic Chloride.** By G. MCGOWAN (*J. pr. Chem.* [2], **29**, 138—139).—Loew describes the action of aqueous ammonia on trichloromethylsulphonic chloride, stating that nitrogen is liberated from the ammonia, and "that the hydrogen combines with the chlorine according to the equation,"  $3CCl_3.SO_2Cl + 8NH_3 = 3CCl_3.SO_2NH_4 + N_2 + 3NH_4Cl$ . The author has studied the above reaction under the most varying circumstances, and has always found that nitrogen is evolved, and that the ammonium salt of trichloromethylsulphonic acid is formed. By substituting aniline for ammonia the corresponding anilide is obtained. J. I. W.

**Derivatives of Isethionic Acid.** By R. HÜBNER (*Annalen*, **223**, 198—235).—When the product of the action of sulphuric anhydride on ether is poured into water, two layers of liquid are formed. The aqueous solution contains ethionic acid, which is converted into isethionic acid by boiling, and the ethereal solution contains hydrogen ethyl sulphate, ethyl methionate, and ethionate.

The first product of the action of sulphuric anhydride on ether is ethyl sulphate, which is converted into hydrogen ethyl sulphate, carbyl sulphate, and ethionic acid by the prolonged action of the sulphuric anhydride. In order to avoid the formation of methionic acid, the sulphuric anhydride vapours are passed into ether at  $0^\circ$ , until the ethereal layer sinks when poured into water. The whole of the product is then poured into water, and the ethyl sulphate is quickly washed, dried, and again treated with sulphuric anhydride. The aqueous solutions are boiled and neutralised with barium carbonate, to convert the ethionic acid into barium isethionate.

The following salts of monochlorethanesulphonic acid,



which was first obtained by Kolbe (*Annalen*, **122**, 38), have been prepared: the *barium* salt,  $(C_2H_4ClSO_3)_2Ba + H_2O$ , crystallises in monoclinic plates, the *lead* salt in prisms containing 2 mols.  $H_2O$ , the *ammonium* salt in anhydrous monoclinic prisms. The *copper* and *zinc* salts form monoclinic plates, containing 3 and 4 mols.  $H_2O$  respectively. The *sodium* salt crystallises in deliquescent plates, containing 1 mol.  $H_2O$ . The *potassium* salt forms anhydrous needles. The *magnesium*, *manganese*, and *ferrous* salts contain 4 mols.  $H_2O$ . The *calcium* salt contains 2 mols.  $H_2O$ .

The *sodium* salt of *monethoxyethanesulphonic acid*,  $EtO.(CH_2)_2.SO_3H$ , is formed by the action of chloroethanesulphonic chloride,



(1 mol.), on an alcoholic solution of sodium ethylate (3 mols.), and also by acting on sodium chlorethanesulphonate with an equivalent quantity of an alcoholic solution of sodium ethylate. The barium salt of ethoxyethanesulphonic acid,  $(C_4H_9SO_4)_2Ba + H_2O$ , crystallises in colourless needles, freely soluble in water. The lead salt forms anhydrous plates, the potassium salt anhydrous prisms, the zinc salt hygroscopic plates containing 6 mols.  $H_2O$ , and the copper salt non-hygroscopic plates containing 6 mols.  $H_2O$ . The sodium salt crystallises in small prisms containing  $\frac{1}{2}$  mol.  $H_2O$ . The free acid was obtained as a thick syrup (sp. gr. 1.359 at  $21^\circ$ ), which appears to be capable of crystallisation.

The *ethylic* salt of *ethoxyethanesulphonic acid*,  $EtO.C_2H_4.SO_3Et$ , is obtained by acting on chlorethanesulphonic chloride (diluted with ether) with dry sodium ethylate.

*Ethoxyethanemonethyldisulphuric acid*, obtained in attempting to prepare ethoxyethanesulphonic acid by the action of sulphuric acid and alcohol on the sodium salt, forms a series of salts which are very soluble in water. Many of them, *e.g.*, those of ammonium and zinc, are very hygroscopic. The barium salt forms silky scales containing 1 mol.  $H_2O$ . The lead salt crystallises in anhydrous needles. The copper salt crystallises with 4 mols.  $H_2O$ . The acid is metameric with Engelke's diethylisethiondisulphonic acid (*Annalen*, **218**, 269). It is, however, dibasic, whilst Engelke's acid is monobasic. It is decomposed by prolonged boiling with water, yielding alcohol, sulphuric acid and ethoxyethanesulphonic acid.

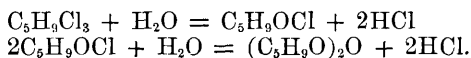
W. C. W.

**Action of Chlorine on Sulphonic Derivatives and Organic Oxy-sulphides.** By W. SPRING and C. WINSSINGER (*Ber.* **17**, 537—540).—In continuing their investigation of the action of chlorine on sulphonic derivatives (Abstr., 1882, 938; *ibid.*, 1883, 659), the authors find that in a strong light chlorine reacts with amylsulphonic acid, forming *monochloramylsulphonic acid* and a chlorinated derivative of amyl. The continued action of chlorine expels the sulphonic group. When amylsulphonic acid is heated in sealed tubes with iodine trichloride it gives *monochloramylsulphonic acid*, *trichloropentane*,  $C_5H_9Cl_3$ , *tetrachloropentane*,  $C_5H_8Cl_4$ , and *chlorosulphonic acid*. When an excess of iodine trichloride is employed, then *mono-* and *di-chloramylsulphonic acids* are formed together with amylene chlorides,  $C_2Cl_6$ ,  $C_2Cl_4$ , sulphonic chloride, and hydrochloric acid. The formation of a dichlor- and the non-formation of a trichlor-amylsulphonic acid show how the introduction of a third atom of chlorine brings about the expulsion of the sulphonic group.

Diamylsulphone is but little acted on by chlorine even in sunlight, whereas, when heated with iodine trichloride, it yields *monochlorodiamylsulphone*,  $C_5H_{10}Cl.SO_2.C_5H_{11}$ , boiling at  $330^\circ$ , *dichlorodiamylsulphone*,  $(C_5H_{10}Cl_2)_2SO_2$  or  $C_5H_9Cl_2.SO_2.C_5H_{11}$ , and a considerable quantity of the *amylene tri-* and *tetra-chlorides*, together with sulphonic chloride. Here also the sulphonic group can exist even in presence of two chlorine-atoms.

Chlorine in presence of water reacts with amyl oxy-sulphide,

(C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>SO, forming *amylsulphonic chloride*, C<sub>5</sub>H<sub>11</sub>.SO<sub>2</sub>Cl, *amylsulphonic acid*, *monochloroamylsulphonic acid*, *diamylsulphone*, *valeraldehyde*, *valeric acid*, *monochlorovaleric acid*, *valeric chloride*, a mixture of *amylene tri- and tetra-chlorides* and hydrochloric acid. The derivatives of valeric acid owe their production to the action of the amylene tri- and tetra-chlorides, thus :



The action of chlorine on amyl oxysulphide may be represented by the following equations :—

- (1.) (C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>SO + 4Cl<sub>2</sub> + H<sub>2</sub>O = C<sub>5</sub>H<sub>11</sub>.SO<sub>2</sub>Cl + C<sub>5</sub>H<sub>9</sub>Cl<sub>3</sub> + 4HCl.
- (2.) (C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>SO + Cl<sub>2</sub> + H<sub>2</sub>O = (C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>SO<sub>2</sub> + 2HCl.
- (3.) C<sub>5</sub>H<sub>11</sub>.SO<sub>2</sub>Cl + H<sub>2</sub>O = C<sub>5</sub>H<sub>11</sub>.SO<sub>3</sub>H + 2HCl.
- (4.) C<sub>5</sub>H<sub>9</sub>Cl<sub>3</sub> + H<sub>2</sub>O (*vide* above).

The amylsulpho-compounds have a greater tendency to form chlorinated derivatives than their lower homologues. P. P. B.

**Derivatives of Uric Acid.** By F. MYLIUS (*Ber.*, 17, 517—527).—*Sarcosine-uric Acid*, C<sub>8</sub>H<sub>9</sub>N<sub>5</sub>O<sub>4</sub>.—This compound, described by Baumann (*Ber.*, 7, 1152), is easily prepared by heating 2 parts of a mixture of uric acid and 3 of sarcosine at 210°. It crystallises from water in colourless crystals containing 2 mols. H<sub>2</sub>O. It gives the murexide reaction, reduces alkaline copper solutions slowly, and is oxidised by potassium permanganate. It possesses both basic and acid characters, forming an unstable acetate and formate, and its ammoniacal solutions are precipitated by silver nitrate and lead acetate. When its solution in potassium hydroxide is heated at 110°, it is resolved into uric acid and sarcosine. Its constitution is expressed by the formula C<sub>8</sub>H<sub>3</sub>N<sub>4</sub>O<sub>3</sub>.CO.CH<sub>2</sub>.NHMe.

*Bromosarcosine-mesouric acid*, C<sub>8</sub>H<sub>7</sub>N<sub>4</sub>O<sub>5</sub>Br, is forming by digesting the aqueous solution of sarcosine-uric acid with bromine; its formation is represented as follows :—C<sub>8</sub>H<sub>9</sub>N<sub>5</sub>O<sub>4</sub> + 2Br + H<sub>2</sub>O = C<sub>8</sub>H<sub>7</sub>N<sub>4</sub>O<sub>5</sub>Br + NH<sub>4</sub>Br. The bromine in this compound is in the same active condition as in the bromo-derivatives of the acid amides (Hofmann, *Abstr.*, 1882, 950, 1052); it is easily replaced by hydrogen, *e.g.*, by treatment with hydrogen sulphide or ammonia, thus :—



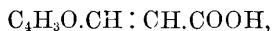
Acids are without action on this bromide, but it exhibits acid characters; it dissolves, for instance, in baryta-water, and is reprecipitated by acids. If, however, a large excess of baryta-water is used, it is decomposed, barium bromide and an insoluble barium salt being formed. The bromine in this compound most probably replaces an

atom of hydrogen in the sarcosine group, and to it the author assigns the constitution  $C_5H_7N_3O_4.CO.CH_2.NBrMe$ .

*Sarcosine-mesouric acid* is the acid obtained by the action of reducing agents on the bromide. It resembles sarcosine-uric acid, differing from it in being more easily soluble in water. It crystallises in rhombic tables or needles, and is insoluble in alcohol. It forms salts with acetic and formic acids, and also with bases; its silver salt,  $C_5H_6N_4O_5Ag_2$ , is formed on adding ammonia to a mixture of silver nitrate and its ammonium salt. It is a powerful reducing agent, reducing solutions of salts of gold and alkaline copper solutions. When oxidised by potassium permanganate, it yields a mixture of acids containing some oxalic acid. Treated with bromine-water, it yields the bromosarcosine-mesouric acid, and a corresponding chlorine compound when treated with chlorine-water. It yields sarcosine when fused with potash.

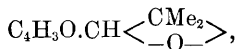
P. P. B.

**Action of Nitrous Acid on Furfurbutylene.** By P. TOENNIES and A. STAUB (*Ber.*, **17**, 850—858).—The boiling point of pure isobutyric anhydride is  $181.5^\circ$ , and its sp. gr. is  $0.9574$  at  $16.5^\circ$ . By the action of furfuraldehyde on isobutyric anhydride and sodium acetate, furfurbutylene,  $C_4H_3O.CH:CMe_2$ , is obtained; its boiling point is  $153^\circ$ , and its sp. gr. is  $0.9509$  at  $14.5^\circ$ . Some furfuracrylic acid,

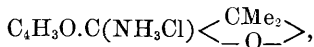


is also formed during the reaction, so that a portion of the sodium acetate and isobutyric anhydride must react to form acetic anhydride, which gives rise to the furfuracrylic acid; consequently sodium acetate can only be used in Perkin's reaction when the anhydride employed is acetic anhydride.

An acetic solution of furfurbutylene, mixed with sodium nitrite and then poured into a strong caustic soda solution, yields a yellow crystalline mass, melting at  $94^\circ$ . It is  $C_4H_3O.CH<\overset{CMe_2}{N_2O_3}>$ . When this compound is gradually added to tin and hydrochloric acid it yields two reduction-products. One of these, *furfurbutylene oxide*,



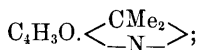
is an oil which volatilises easily, it is soluble in water, boils at  $186^\circ$ , and does not change in the air; it does not react with acetic anhydride, so that it contains no hydroxyl-group, neither does it give any of the reactions of the ketones. The residual solution from which the furfurbutylene oxide has separated, after the tin has been removed and the solution concentrated, gives crystals of the composition



and yielding a well-crystallised platinochloride. Its reactions are those of a primary amine. When it is boiled with tin and hydrochloric acid, ammonium chloride and furfurbutylene oxide are formed;



this explains the formation of the oxide during the first reduction. On treating the hydrochloride with acetic anhydride it yields an acetyl-derivative, melting at  $153^{\circ}$  and boiling at  $305\text{--}310^{\circ}$ . Strong caustic soda solution added to the hydrochloride separates the free base,  $\text{C}_4\text{H}_3\text{O}.\text{C}(\text{NH}_2)\text{<}\frac{\text{CMe}_2}{\text{O}}\text{>}$ , an oil soluble in water and having a feeble odour. It boils at  $215\text{--}220^{\circ}$ , and distils easily with aqueous vapour: in both cases it loses part of its water, leaving a base,



this is crystalline, easily soluble in water and volatilises with steam; it melts at  $142^{\circ}$  and boils at  $300\text{--}310^{\circ}$ . With acetic anhydride and nitrous acid it reacts as a tertiary base. The solution of the hydrochloride is decomposed on boiling; it yields a well-crystallised platino-chloride.  
H. B.

**The Thiophene-group.** By L. WEITZ (*Ber.*, **17**, 792—801).—A sample of benzene that had been purified *only* by distillation, and had never been treated with acid, was examined for contained thiophene; but it was found to contain no more thiophene than ordinary benzene. The distillation of the crude lead thiophenesulphonate and ammonium chloride is best carried out in an iron retort.

Thiophene when treated with chlorine (comp. Abstr., 1883, 1091) readily yields a mixture of the *monochlorothiophene*,  $\text{C}_4\text{H}_3\text{ClS}$ , and the *dichlorothiophene*,  $\text{C}_4\text{H}_2\text{Cl}_2\text{S}$ , which are separated and purified by distillation; they boil at  $130^{\circ}$  and  $170^{\circ}$  respectively. The *tetrachlorothiophene* is formed by passing chlorine through the dibromide; when pure it forms large crystals melting at  $35^{\circ}$ .

The following salts of thiophenesulphonic acid have been examined:— $\text{C}_4\text{H}_3\text{S}.\text{SO}_3\text{Na} + \text{H}_2\text{O}$ ;  $(\text{C}_4\text{H}_3\text{S}.\text{SO}_3)_2\text{Ba} + 3\text{H}_2\text{O}$ ;  $\text{C}_4\text{H}_3\text{S}.\text{SO}_3\text{Ag} + 3\text{H}_2\text{O}$ ;  $(\text{C}_4\text{H}_3\text{S}.\text{SO}_3)_2\text{Pb} + \text{H}_2\text{O}$ ;  $(\text{C}_4\text{H}_3\text{S}.\text{SO}_3)_2\text{Ca} + ?\text{H}_2\text{O}$ ; they are very soluble in water, and some are hygroscopic. *Thiophenesulphonic chloride*,  $\text{C}_4\text{S}_3\text{S}.\text{SO}_2\text{Cl}$ , is formed by the action of phosphorous chloride on the sodium salt; it is a liquid boiling at over  $200^{\circ}$ , with decomposition, and not readily decomposed by water. On one occasion, crystals were formed melting at  $28^{\circ}$  and boiling without decomposition; they had the same composition as the liquid chloride. When an alcoholic solution of thiophenesulphamide is treated with silver nitrate and ammonia, it deposits *silver thiophenesulphamate*,  $\text{C}_4\text{H}_3\text{S}.\text{SO}_2.\text{NHAg}$ , in iridescent scales. Aniline acts on thiophenesulphonic chloride to form *thiophenesulphanilide*,  $\text{C}_4\text{H}_3\text{S}.\text{SO}_2.\text{NHPh}$ , crystallising from ether and melting at  $96^{\circ}$ . Sodium ethylate acts on the chloride to form the *ethylic thiophenesulphonate*,  $\text{C}_4\text{H}_2\text{S}.\text{SO}_3\text{Et}$ , a yellowish oil. The zinc salt of *thiophenesulphinic acid* is formed when an alcoholic solution of thiophenesulphonic chloride is treated with zinc-dust. The product is washed with water to remove zinc chloride, the zinc thiophenesulphinate converted into the sodium salt by sodium carbonate, and the solution after removal of the zinc carbonate by filtration is concentrated, acidified with hydrochloric acid,

and extracted with ether; the free acid crystallises in needles when exposed over sulphuric acid in a vacuum; it melts at  $67^{\circ}$ . The salts,  $C_4H_3S.SO_2Ag$ ,  $(C_4H_3S.SO_2)_2Ba + 2H_2O$ , and  $(C_4H_3S.SO_2)_2Zn + 3H_2O$ , are described.

All these derivatives have the strongest resemblance to the corresponding benzene-derivatives, but are distinguished by giving the indophenine reaction.

H. B.

**Homologues of Thiophene.** By V. MEYER and H. KREIS (*Ber.*, 17, 1558—1563).—V. Meyer and G. Dyson find that iodine and iodic acid, or, still better, iodine and mercuric oxide, act on thiophene even at ordinary temperatures. Iodine, in the calculated proportion, is added to crude thiophene, and then mercuric oxide added gradually, without cooling, until all the iodine is dissolved. By varying the amount of iodine used, polysubstituted compounds can be obtained. *Moniodothiophene*,  $C_4H_3SI$ , is a colourless oil, boiling at  $182^{\circ}$  uncorr., and resembling iodobenzene in all its properties. *Diiodothiophene* forms white crystals melting at  $40.5^{\circ}$ .

Making use of moniodothiophene thus prepared, the authors have synthesised several homologues of thiophene by the Würz-Fittig method. The directions given by Fittig and König (*Annalen*, 144, 278) for the preparation of homologues of benzene were exactly followed. The following compounds were obtained:—

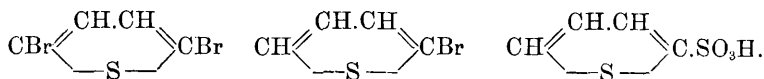
	B. p.	Rel. density.
Methylthiophene (thiotolene), $C_4H_3SMe$	$113^{\circ}$	1.019
Ethylthiophene, $C_4H_3SEt$ .....	$132-134^{\circ}$	0.990 at $24^{\circ}$ .
Propylthiophene (norm.), $C_4H_3SPr$ ..	$157.5-159.5^{\circ}$	0.974 „ $16^{\circ}$ .
Butylthiophene (norm.), $C_4H_3S.Bu$ ..	$181-182^{\circ}$	0.957 „ $19^{\circ}$ .

All show Laubenheimer's reaction, but a *very* little only must be taken (a drop on a glass rod), and diluted with much water, otherwise brown resinous compounds are formed. The tint obtained in the reaction becomes blue in the higher homologues. All resemble the corresponding benzene-derivatives very closely both in boiling point and properties. The authors have not yet determined as to whether the above methylthiophene is identical with that isolated from coal-tar oils.

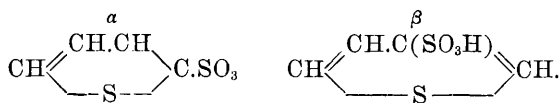
L. T. T.

**Isomerism in the Thiophene Series.** By V. MEYER (*Ber.*, 17, 1563—1566).—If the formula  $CH \begin{array}{c} \text{CH.CH} \\ \diagup \quad \diagdown \\ \text{---S---} \end{array} CH$ , proposed by the

author be correct, thiophene should yield two series of monosubstitution compounds. The great analogy between benzene and thiophene in the formation of substitution-products renders it probable that in *dibromothiophene* the two bromine-atoms are in the positions which are separated by the greatest number of carbon-atoms, and that consequently in the monosubstitution-derivatives with negative radicals the radical is attached to the carbon nearest to the sulphur atom.



In this case, the sulphonic acid obtained from dibromothiophene should yield, when dibrominated, a monosulphonic acid isomeric with that obtained by the direct sulphonation of thiophene. This is indeed the case; Langer's acid (next page) is isomeric with the  $\alpha$ -acid previously described. The formation of an anhydride from Langer's dibromothiophenedisulphonic acid points—from analogy with phthalic acid—to the two sulphonyl-groups being on neighbouring carbons, which would also be the case if the above view of the constitution of thiophene be correct. The constitution of the  $\alpha$ - and  $\beta$ -acid would then be—



L. T. T.

**Dithienyl.** By R. NAHNSEN (*Ber.*, **17**, 789—790).—By passing thiophene through a tube heated just to redness, condensation takes place as with the benzene hydrocarbons, and *dithienyl*,  $(\text{C}_4\text{H}_3\text{S})_2$ , is formed. It crystallises from alcohol in white plates melting at  $83^\circ$ . With isatin and sulphuric acid it gives a deep-blue coloration. A mixture of benzene and thiophene passed through a red-hot tube does not yield pure dithienyl, but a mixture probably of diphenyl and the bodies  $\text{C}_6\text{H}_5$ ,  $\text{C}_4\text{H}_3\text{S}$  and  $(\text{C}_4\text{H}_3\text{S})_2$ .

H. B.

**Substances accompanying Toluene from Coal-tar.** By V. MEYER and H. KREIS (*Ber.*, **17**, 787—789).—It was previously shown (*Abstr.*, 1883, 1092, and this vol. p. 586) that coal-tar toluene contains the next higher homologue of thiophene, and the substitution-product,  $\text{C}_4\text{HMeBr}_2\text{S}$ , was isolated. This body when treated with bromine in excess in the cold yields tribromothioltolene,  $\text{C}_4\text{MeBr}_3\text{S}$ , a white crystalline substance melting at  $74^\circ$ .

The separation of the thioltolene from the crude product containing 15 per cent. thioltolene and 85 per cent. toluene, cannot be effected by repeated treatment with strong sulphuric acid. But whereas the benzene hydrocarbons are only acted on by iodine and iodic acid or iodine and mercuric oxide when heated, thiophene and its homologues are readily acted on at the ordinary temperature. The product of the reaction is extracted with ether and the solution fractionated; at  $180^\circ$  there remains an iodothioltolene which cannot be distilled without decomposition; the residue is dissolved in alcohol and treated with sodium; addition of water causes the separation of an oil, which is dried over calcium chloride and rectified. This is pure *thioltolene*, a colourless mobile liquid boiling constantly at  $113^\circ$ , and of sp. gr. 1.0194 at  $18^\circ$ . The authors are now preparing the next homologue—*thioxytolene*.

H. B.

**Isomeric Thiophenesulphonic Acids.** By J. LANGER (*Ber.*, **17**, 1566—1570).—This research was undertaken with the view of throwing light on the constitution of thiophene (see also this vol., p. 1131). *Dibromothiophenesulphonic acid*,  $C_4HSBr_2SO_3H$ , was prepared by treating dibromothiophene, boiling at  $205-207^\circ$ , with pyrosulphuric acid ( $H_2S_2O_7$ ). The free acid was not examined. Its *lead salt*,  $(C_4SHBr_2SO_3)_2Pb + 5\frac{1}{2}H_2O$ , crystallises from water in small white lustrous crystals, and was debrominated by treating its aqueous solution with sodium amalgam. The sulphonic acid was purified by conversion into its chloride.  $\beta$ -Thiophenesulphonic chloride,  $C_4SH_3SO_2Cl$ , forms large colourless crystals melting at  $43^\circ$ , and having an odour similar to that of benzenesulphonic chloride. It appears to distil undecomposed. The chloride of the  $\alpha$ -sulphonic acid (obtained directly from thiophene) is liquid.  $\beta$ -Thiophenesulphonamide,  $C_4SH_3SO_2NH_2$ , was prepared by the action of ammonium carbonate on the chloride. It crystallises in lustrous plates which differ in appearance from those of the amide of the  $\alpha$ -acid. It melts at  $148^\circ$ , whereas the  $\alpha$ -derivative melts at  $142^\circ$ . It gives a deep-blue solution when heated with isatin and sulphuric acid. It is thus clear that the  $\alpha$ - and  $\beta$ -sulphonic acids are isomeric and not identical.

*Dibromothiophenedisulphonic acid*,  $C_4SBr_2(SO_3H)_2$ , was obtained by acting on dibromothiophene with a large excess of pyrosulphuric acid. It crystallises in shining white scales which when heated above  $150^\circ$  turn brown, and above  $200^\circ$  are partly decomposed and become liquid. This liquid is undoubtedly the *anhydride* of the disulphonic acid, and is reconverted into the acid by boiling with alkalis or with barium hydroxide.

L. T. T.

**Wachendorff's Chloronitrotoluene.** By E. LELLMANN (*Ber.*, **17**, 534—537).—Wachendorff (*Annalen*, **185**, 273), by treating paranitrotoluene with antimony pentachloride, obtained a chloronitrotoluene, which he regarded as  $C_6H_3MeCl.NO_2$  [1:3:4], since it yielded a chloronitrobenzoic acid identical with that obtained by Hübner from metachlorobenzoic acid. The author has prepared this chloronitrotoluene and converted it into the corresponding toluidine, which, if Wachendorff's conclusions be correct, should be identical with Wroblewsky's, obtained from para-acetotoluidine (*Annalen*, **168**, 196). A comparison, however, shows it to be distinct; this base boils at  $237-238.5^\circ$ , and solidifies at  $10-12^\circ$ , whilst Wroblewsky's base boils at  $222^\circ$ . Moreover, this compound, when submitted to the diazo-reaction, is converted into chlorotoluene, and the latter by oxidation into orthochlorobenzoic acid melting at  $136.5^\circ$ . From this the author concludes that Wachendorff's chloronitrotoluene contains the chlorine in the ortho-position.

P. P. B.

**Action of Copper on Benzotrichloride, Benzal Chloride, and Benzyl Chloride.** By A. ONUFROWICZ (*Ber.*, **17**, 833—837).—Benzenyl trichloride, heated with copper at  $100^\circ$ , yields a solid mass, which leaves a white crystalline product when extracted with alcohol or benzene, toluene tetrachloride ( $C_6H_5.CCl_2$ )<sub>2</sub>. Hanhart has previously prepared

tolane dichloride by this same method, but it is only a secondary product, as tolane tetrachloride yields the dichloride when heated with copper.

If benzal dichloride is heated with copper, and the mass extracted with benzene, it yields crystals of stilbene chloride,  $(C_6H_5.CHCl)_2$ , melting at  $180^\circ$ .

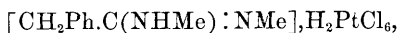
Benzyl chloride, when heated with copper, does not act until a temperature of  $150$ — $160^\circ$  is reached. The product contains dibenzyl if the quantity of copper employed is not too large; with excess of copper and access of air, a resinous mass is obtained. H. B.

**Derivatives of Benzyl Cyanide.** By G. LUCKENBACH (*Ber.*, 17, 1421—1428).—By the action of hydrochloric acid gas on a well-cooled mixture of equal molecular proportions of absolute alcohol and benzyl cyanide, there is first formed the compound  $CH_2Ph.CCl(NH_3Cl).OEt$ , which, on standing in a flat porcelain dish over sodium hydroxide for a few days, is converted into *phenylacetimidoethyl-ether hydrochloride*,  $CH_2Ph.C(OEt) : NH_3.HCl$ . This crystallises in concentric groups of flat needles, softens at  $60^\circ$ , and is completely fused at  $85^\circ$ , and then decomposes into phenylacetamide and ethyl chloride, is readily soluble in alcohol and water, nearly insoluble in benzene and ether, and is very deliquescent. The platinochloride crystallises in prisms, and decomposes readily. The free *imido-ether*,  $CH_2Ph.C(OEt) : NH$ , obtained by the action of concentrated soda on the hydrochloride, forms a colourless liquid of agreeable aromatic odour; on distillation, it decomposes into benzyl cyanide and alcohol. The corresponding methyl ether and its hydrochloride were also prepared; they closely resemble the ethyl compounds, but are still more unstable.

*Phenylacetimido acetate*,  $CH_2Ph.C(OAc) : NH$ , prepared by the action of acetic anhydride on phenylacetimido-ether, crystallises in slender white needles, melts at  $129^\circ$ , is sparingly soluble in cold water, more readily soluble in hot water, readily soluble in alcohol.

*Phenylacetamidine*,  $CH_2Ph.C(NH_2) : NH$  (comp. Bernthsen, this Journal, 1870 [ii], 95). On adding a solution of ammonia to phenylacetimido-ether hydrochloride, the free imido-ether is at first formed, whilst ammonium chloride separates; on standing for some days, however, with occasional shaking, the precipitate disappears, and the solution then contains traces of ethyl phenylacetate, together with *phenylacetamidine hydrochloride*. The latter crystallises in long flat needles of the formula  $CH_2Ph.C(NH_2) : NH_3.HCl + H_2O$ , and is readily soluble in water and alcohol. The free base, prepared by rubbing the chloride with concentrated caustic soda, drying the resulting paste in a vacuum and extracting with benzene, still somewhat impure, crystallises in lustrous flat needles or plates, melts at  $108$ — $112^\circ$ , is readily soluble in water and alcohol, sparingly soluble in ether and benzene. The platinochloride crystallises in long flat needles. By heating phenylacetamidine with acetic anhydride and sodium acetate, it yields phenylacetimido acetate; with cold acetic anhydride, on the other hand, it gives in addition a diacetyl compound,  $CH_2Ph.C(NHAc) : NAc$ , crystallising in very brilliant small tetragonal plates, melting at  $172$ — $173^\circ$ , soluble in hot water, sparingly soluble in alcohol and cold water, nearly insoluble in ether.

*Symmetrical dimethylphenylacetamidine*,  $\text{CH}_2\text{Ph.C(NHMe):NMe}$ , separates as hydrochloride after some days' standing from a mixture of phenylacetimido-ether hydrochloride with an alcoholic solution of methylamine. The free base is an oil which crystallises on long standing over sulphuric acid. The hydrochloride crystallises in hexagonal pyramids. The platinochloride,



forms small crystals, apparently rhombic; it is more soluble in alcohol than in water.

*Unsymmetrical dimethylphenylacetamidine hydrochloride*, prepared from dimethylamine and phenylacetimido-ether hydrochloride, is crystalline. The platinochloride,  $[\text{CH}_2\text{Ph.C(NMe}_2\text{):NH}]_2\text{H}_2\text{PtCl}_6$ , crystallises in feathery groups of needles.

*Diethylphenylacetamidine hydrochloride*, prepared in similar manner by means of ethylamine, is not crystalline; the platinochloride forms a red resinous mass; the free base appears to be less soluble in ether than the methyl compound.

*Diphenyl-phenylacetamidine*,  $\text{CH}_2\text{Ph.C(NHPh):NPh}$ , is prepared by heating a mixture of aniline and phenylacetimido-ether hydrochloride for some time at  $60^\circ$ . It crystallises in flat needles and plates, melts at  $107\text{--}108^\circ$ , is readily soluble in alcohol, nearly insoluble in water. The platinochloride crystallises in small plates.

A. J. G.

**Oxidation of Mercury Diethyl with Potassium Permanganate.** By M. SEIDEL (*J. pr. Chem.* [2], 29, 134—136).—When mercury diethyl is heated with a concentrated aqueous solution of potassium permanganate, it is readily oxidised. On adding hydrochloric acid to the strongly alkaline solution, a white precipitate is obtained, consisting of ethyl mercuric chloride,  $\text{HgEtCl}$ , crystallising from alcohol in silvery plates melting at  $190^\circ$ . It is probable that in the above reaction mercuric ethyl hydroxide is first formed; but the hydroxyl-group is replaced by chlorine on treatment with hydrochloric acid.

Mercury-dimethyl in like manner yields mercuric methyl chloride, which crystallises in lustrous prisms melting at  $170^\circ$ . J. I. W.

**Action of Potassium Permanganate on Mercury-diphenyl: a Correction.** By R. OTTO (*J. pr. Chem.* [2], 29, 136—138).—It is stated in a former paper that when the product obtained by oxidising mercury-diphenyl with potassium permanganate is precipitated, by adding hydrochloric acid, the compound  $\text{C}_6\text{H}_5\text{.HgO.OH}$ , is thrown down in small lustrous crystals melting at  $251\text{--}252^\circ$ . The precipitate, however, consists of the *chloride*,  $\text{HgPhCl}$ . The hydroxide can be isolated by shaking the products of the reaction with benzene before the addition of hydrochloric acid.

Mercury-dilotyl resembles the diphenyl compound in the foregoing properties, the compounds  $\text{HgC}_7\text{H}_7\text{.OH}$  and  $\text{HgC}_7\text{H}_7\text{Cl}$  being formed.

J. I. W.

**Tolylstibine.** By A. MICHAELIS and U. GENZKEN (*Ber.*, 17, 924—925).—Antimony tribromide, paramonobromotoluene, and sodium, in

presence of benzene, readily react to form *paratolystibine*,  $(C_6H_4Me)_3Sb$ , a crystalline substance melting at  $127.5^\circ$ .

When dissolved in light petroleum and treated with the halogens, the additive compounds,  $(C_7H_7)_3SbCl_2$ , &c., crystallise out, melting at  $156.5^\circ$  (chloride),  $233^\circ$  (bromide), and  $182.5^\circ$  (iodide). The bromide treated with caustic soda yields *paratritolylstibine oxide*,  $(C_7H_7)_3SbO$ , melting at  $223.5^\circ$ . If the oxide is dissolved in hot acetic acid, and some water added, it deposits the crystalline *tritolystibine hydroxide*,  $(C_7H_7)_3Sb(OH)_2$ , as it cools; this melts at  $169.5^\circ$ . *Orthotolylstibine* has not yet been obtained in a crystalline state. *Metatritolylstibine* separates from alcohol and ether in crystals melting at  $64.5^\circ$ . The dibromide melts at  $113^\circ$ , and is easily soluble in ether; its isomerides are almost insoluble.

H. B.

**Electrolyses and Electrosyntheses.** By E. DRECHSEL (*J. pr. Chem.* [2], **29**, 229—252).—The author has previously (Abstr., 1881, 192) shown that by electrolysing a solution of ammonium carbamate with an alternating current carbamide is formed by the abstraction of the elements of water. It was observed that the platinum electrodes were strongly attacked with formation of platinum bases (Gerdes, Abstr., 1883, 27). By passing the current through a saturated solution of potassium carbonate large quantities of spongy platinum may be prepared. Palladium electrodes with a solution of ammonium carbamate gave no bases, scarcely any of the metal being dissolved. Similar phenomena have been observed by De la Rive (*Pogg. Ann.*, **141**, 152; **145**, 163, 407), who found that gas was disengaged if the electrodes offered only a small surface, whilst with large surfaces but little gas is given off, and the surfaces become covered with a film of the metal (Pt, Pb, Au, Ag, Cu, Pb). Planté (*Jahresb.*, 1866, 98) has also noticed the evolution of oxygen containing ozone from easily oxidisable electrodes. The author, with a view to synthesising phenolsulphuric acid, subjected a mixture of magnesium bicarbonate and sulphate dissolved in water and then saturated with pure commercial phenol, to an alternating current for 30 hours. The electrodes consisted of three large pieces of platinum foil to each pole. A number of products were formed by the action, but mostly in quantities insufficient for analysis. The action of the alternating current may be regarded as inducing alternate oxidation and reduction, the former giving rise to synthetical, and the latter to analytical changes. As products of synthesis there were found  $\gamma$ -diphenol and phenolsulphuric acid, and by oxidation of a single molecule of phenol, quinol, and catechol, were formed, the former in larger quantity than the latter; apparently the catechol suffers further oxidation with formation of acids of the acetic and oxalic series, probably normal valeric and butyric acids, as well as formic acid, whilst the dibasic acids found were succinic, oxalic, and probably also malonic acid. The author points out that some of these substances have not hitherto been obtained directly from phenol, thus neither  $\gamma$ -diphenol, quinol, nor catechol are produced by the action of ordinary oxidising agents, but the author suggests that their formation is in one respect similar to that of catechol by fusing phenol with sodium hydroxide, for in

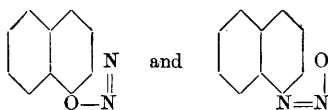
both cases the oxidation takes place in the presence of a strong reducing agent, viz., nascent hydrogen. The acid sulphates of phenol, quinol, and catechol are also formed from phenol in the animal system, but as the whole of the phenol taken into the system is not thus accounted for, a further examination of phenolic urine for some of the other acids, found in the above action, is required, especially for succinic acid.

P. F. F.

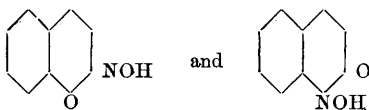
**Nitrosophenols.** By H. GOLDSCHMIDT (*Ber.*, **17**, 801—805).—In a former paper (this vol., 735) it has been shown that the so-called nitrosophenols are formed by the action of hydroxylamine on the quinones, and in all probability therefore they are quinone oximides. It is now shown that  $\alpha$ -nitroso- $\beta$ -naphthol and  $\beta$ -nitroso- $\alpha$ -naphthol are oximido-derivatives.

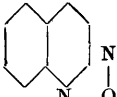
The  $\beta$ -nitroso- $\alpha$ -naphthol prepared from  $\beta$ -naphthoquinone has already been described (*loc. cit.*), as also the product  $C_{10}H_8N_2O$ , crystallising in colourless needles melting at  $77^\circ$ , obtained by further heating with hydroxylamine.

The  $\alpha$ -nitroso- $\beta$ -naphthol was prepared from  $\beta$ -naphthol and amyl nitrite according to Walker's method (*Ber.*, **17**, 399); the body,  $C_{10}H_8N_2O$ , obtained from it by the action of hydroxylamine, melts at  $78^\circ$ . Assuming the usual formulæ for  $\beta$ -nitroso- $\alpha$ -naphthol and  $\alpha$ -nitroso- $\beta$ -naphthol, it follows that by the further action of hydroxylamine two isomeric bodies would be formed—



whereas if the bodies have the constitutions here proposed, viz. :—

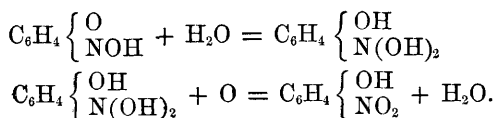


the same body  will be formed in both cases.

Experiment proved that the two products,  $C_{10}H_8N_2O$ , are identical, their composition, melting point, and crystalline form all being the same, as also their behaviour with different solvents. Liebermann having given the name anthrone to the group  $C_{14}H_{10}O$ , the name  $\alpha$ - or  $\beta$ -naphthone may be given to the group  $C_{10}H_8O$ , and the “nitroso-naphthols” will then be called  $\beta$ -isonitroso- $\alpha$ -naphthone and  $\alpha$ -isonitroso- $\beta$ -naphthone. Both these bodies yield hydroxylamine when heated with strong hydrochloric acid. The conversion of these



"nitrosophenols" into nitrophenols by oxidation may be expressed, assuming two reactions to take place:—



H. B.

**Carvol.** By H. GOLDSCHMIDT (*Ber.*, **17**, 1577—1579).—Carvol and hydroxylamine yield *carvoxime*,  $\text{C}_{10}\text{H}_{14}:\text{NOH}$ , which crystallises in white scales melting at  $66\cdot5^\circ$ . With phenylhydrazine it yields *carvol-phenylhydrazine*,  $\text{C}_{10}\text{H}_{14}:\text{N}_2\text{HPh}$ , crystallising in white needles, which soften at  $100^\circ$  and melt at  $106^\circ$ . It is therefore probable that the

formula  $\text{CMe} \begin{array}{c} \text{CH}\cdot\text{CH} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{CH}_2 \end{array} \text{CPr}$ , first proposed by Fittig, is correct, and not his second and more generally received formula. L. T. T.

**Carroway Oil.** By F. A. FLÜCKIGER (*Arch. Pharm.* [3], **22**, 361—366).—A sample of carvol from H. Haensel, in Pirna, boiled constantly at  $224\text{--}225^\circ$ , and a column of 50 mm. rotated polarised light  $+29\cdot1^\circ$ ; it was free from carvene, and its sp. gr. is  $0\cdot9574$  at  $23\cdot5^\circ$ . The formation of terpin from carvene by the action of nitric acid requires the lapse of several months; carvene is a homogeneous body, for it boils constantly at  $174^\circ$ , its sp. gr. is  $0\cdot849$  at  $15^\circ$ , and the rotation  $+53$  at  $20^\circ$ ; by treatment with sulphuric acid of sp. gr. =  $1\cdot55$  it is converted into a thick syrup and becomes optically inactive.

Oleum carvi, according to the German Pharmacopœia, gives a violet or red coloration with ferric chloride, but the reaction cannot always be observed. Neither the last fractions nor the pitch-like residue obtained in the distillation of carroway oil contain phenols nor give the above reaction. If, however, the fresh and colourless oil be allowed to stand some months, it becomes yellow and gives the ferric chloride reaction; the substance giving the reaction is soluble in soda solution, but its quantity is very small; this substance is not carvacrol, as this gives a green coloration with ferric chloride (*Abstr.*, 1882, 1065). H. B.

**Mixed Ethers of Quinol.** By F. FIALA (*Monatsh. Chem.*, **5**, 232—235).—These compounds were prepared from monomethylquinol by the method used by Hlasiwetz and Habermann for the preparation of dimethylquinol (*this Journal*, 1876, i, 79).

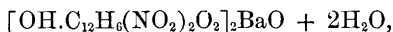
*Methylethylquinol*,  $\text{C}_6\text{H}_4(\text{OMe})\cdot\text{OEt}$ , forms a colourless crystalline mass, of fatty lustre. It has a penetrating fennel-like odour, and burning taste; it melts at  $39^\circ$  (uncorr.). It is readily soluble in benzene, ether, and chloroform, less soluble in absolute alcohol and glacial acetic acid. Like all other dialkyl ethers of quinol, it readily distils with steam.

*Methylpropylquinol*,  $\text{C}_6\text{H}_4(\text{OMe})\cdot\text{OPr}$ , crystallises in colourless plates of agreeable odour, somewhat like that of fennel; it has a burning

taste and melts at  $26^{\circ}$  (uncorr.). It is readily soluble in benzene, ether, chloroform, absolute alcohol, and glacial acetic acid; addition of water completely reprecipitates it from its solution in the two last-named solvents.

*Methylisobutylquinol*,  $C_6H_4(OMe).OBU^{\beta}$ , forms a colourless liquid, heavier than water, of agreeable aromatic odour and burning taste. It distils between  $227-230^{\circ}$ . It is readily soluble in benzene, ether, chloroform, absolute alcohol, and glacial acetic acid. A. J. G.

**Resorcinol Oxide.** By K. HAZURA and P. JULIUS (*Monatsh. Chem.*, 5, 188—192).—*Nitroresorcinol oxide*,  $[C_6H_3(NO_2).OH]_2O$ , is prepared by shaking 1 gram of mononitroresorcinol with  $2\frac{1}{2}$  c.c. of Nordhausen sulphuric acid; after a few seconds the nitroresorcinol dissolves, and the solution is quickly poured into water to prevent further conversion of the oxide into the sulphonic acid; the oxide separates in microscopic needles, whilst nitroresorcinolsulphonic acid remains in solution. Nitroresorcinol oxide can be obtained either in anhydrous pale rose-red needles, or in brownish-red warty crystals of the formula  $[C_6H_3(NO_2).OH]_2O + H_2O$ . It is sparingly soluble in water and alcohol, insoluble in ether, readily soluble in ammonia, but is not reprecipitated on addition of acetic acid. It dissolves in concentrated sulphuric acid, and is reprecipitated on addition of water. When heated, it turns brown at  $170^{\circ}$ , and carbonises without fusion at higher temperatures. The normal barium salt,  $C_{12}H_6(NO_2)_2O_3Ba + 5\frac{1}{2}H_2O$ , crystallises in brownish-yellow needles of nacreous lustre, and is readily soluble in water. The acid barium salt,



crystallises in brownish-yellow needles, and is also readily soluble in water. By the action of concentrated nitric acid, nitroresorcinol oxide is converted into trinitroresorcinol, and another product melting at  $104-105^{\circ}$ .

By heating resorcinoldisulphonic acid (1 mol.) and resorcinol (2 mols.) at  $190^{\circ}$ , a substance is obtained which agrees in all respects with Barth and Weidel's diresorcinol oxide (this Journal, 1876, i, 921). The same compound is also formed by heating phenanthrenedisulphonic acid with resorcinol, the phenanthrenesulphoinresorcinol obtained by Fischer in this reaction (*Abstr.*, 1880, 474) being most probably impure resorcinol oxide. A. J. G.

**Diresorcinol and Diresorcinolphthaleïn.** By R. BENEDIKT and P. JULIUS (*Monatsh. Chem.*, 5, 177—187).—On fusing resorcinol with caustic soda, Barth and Schreder obtained about 1.5 per cent. of diresorcinol, together with 60—70 per cent. of phloroglucinol, but by working on a larger scale, as much as 25—35 per cent. of diresorcinol can be obtained. Pure diresorcinol melts at  $310^{\circ}$ .

*Acetyldiresorcinol*,  $C_{12}H_6(OAc)_4$ , prepared by boiling diresorcinol with acetic anhydride and sodium acetate, crystallises in lustrous prisms and melts at  $152^{\circ}$ . It is soluble in cold nitric acid, and is reprecipitated unaltered on addition of water.

*Hexanitrodiresorcinol*,  $C_{12}(NO_2)_6(OH)_4$ , is prepared by carefully

heating acetyldiresorcinol with fuming nitric acid; it forms lustrous yellow crystals, explodes without previous fusion at about  $230^{\circ}$ , and is readily soluble in water.

*Decabromodiresorcinol*,  $C_{12}Br_{10}O_4$ , prepared by the action of a solution of bromine in concentrated hydrochloric acid on a dilute solution of diresorcinol in potash, forms large crystals; on heating at  $185^{\circ}$  it loses about 2 mols. of bromine, the residue is insoluble in the usual solvents, and on further heating it again evolves bromine, and blackens at  $200$ — $210^{\circ}$ . An impure hexabromodiresorcinol is obtained as a yellowish powder by warming the decabromo-compound with sulphurous acid.

*Diresorcinolphthaleïn* was first prepared by Link (Abstr., 1881, 96), who assigned to it the formula  $C_{32}H_{22}O_{10}$ ; the authors confirm in general his account of the substance, but conclude from the result of their analyses, and from a quantitative study of its formation, that it

has the formula  $C_{20}H_{12}O_6 = \begin{array}{c} C_6H_2(OH)_2 \\ | \\ C_6H_2(OH)_3 \end{array} \begin{array}{c} \diagup \\ C \\ \diagdown \end{array} \begin{array}{c} C_6H_4 \\ \diagdown \\ -O- \end{array} \begin{array}{c} \diagup \\ CO \end{array}$ , and that its

formation is represented by the equation  $C_{12}H_{10}O_4 + C_8H_4O_3 = H_2O + C_{20}H_{12}O_6$ . The deep blue ammoniacal solution of diresorcinolphthaleïn is decolorised by alcohol, whilst the solution in potash is unaffected, even on boiling with that reagent. By the action of bromine on diresorcinolphthaleïn, both in solution in glacial acetic acid, a bromo-derivative is obtained in the form of yellow crystals, soluble in alkalis, with a beautiful blue colour. It could not be purified. An acetyl derivative was obtained as an amorphous resinous mass. *Diresorcinolphthalin* was prepared according to Link's directions. On analysis it yields numbers agreeing better with the formula  $C_{20}H_{14}O_6$  than with  $C_{32}H_{24}O_{10}$ , the formula assigned to it by Link. It crystallises with 2 mols.  $H_2O$ , and melts at  $235^{\circ}$ .

*Insoluble Diresorcinolphthaleïn*,  $C_{32}H_{20}O_9$ .—In the preparation of diresorcinolphthaleïn, there is always formed in small amount a substance insoluble in water, to which the authors give the name of "insoluble diresorcinolphthaleïn;" the largest yield is obtained when two molecular weights of diresorcinol are heated with one of phthalic anhydride. Its formation is most probably represented by the equation  $2C_{12}H_{10}O_4 + C_8H_4O_3 = 2H_2O + C_{32}H_{20}O_9$ . It can be in small part converted into the soluble phthaleïn by fusion with phthalic anhydride, whilst the soluble phthaleïn is almost entirely converted into the insoluble compound by heating it with diresorcinol. By recrystallisation from alcohol, it is obtained as a nearly white, heavy, microcrystalline powder. It commences to decompose when heated to  $240^{\circ}$ .

A. J. G.

**Action of Perthiocyanic Acid on some Aromatic Monamines.** By A. TURSINI (*Ber.*, 17, 584—588).—Glutz (*Annalen*, 154, 44) has shown that aniline and perthiocyanic acid heated together yield a *monophenylthiobiuret*. The author finds that paratoluidine behaves in a similar manner, forming *monotolythiobiuret*,  $C_9H_{11}N_2S_2$ . This compound is soluble in alcohol, from which it crystallises in microscopic needles melting at  $158^{\circ}$ . The thiobiurets possess acid properties,

dissolve in alkalis, and are reprecipitated by acids; they are easily converted into ethyl-derivatives by treating their alcoholic solutions with ammonia and ethyl iodide. *Ethylphenylthiobiuret*,  $C_8H_8N_3S_2Et$ , crystallises from alcohol in rhombic tables melting at  $109^\circ$ , and *ethyltolylthiobiuret* forms large needles melting at  $134^\circ$ . Acetic chloride reacts easily with these compounds, forming acetic derivatives; *acetyltolylthiobiuret* crystallises from alcohol in yellow needles melting at  $166^\circ$ .

Dimethylaniline and perthiocyanic acid react with one another, not, however, to produce substituted thiobiurets, but a base, *tetramethylthioaniline*, similar to the thioaniline described by Merz and Weith (*Ber.*, **4**, 384). *Tetramethylthioaniline*,  $(C_6H_4.NMe_2)_2S$ , crystallises from alcohol in white needles; it is soluble in ether and melts at  $125^\circ$ . It is easily soluble in hydrochloric acid, and the solution gives a yellow precipitate with platinum chloride. The base is unaltered when heated in sealed tubes with concentrated hydrochloric acid, or by fusion with potash. The picrate is the most stable of its salts; it is insoluble in water, but sparingly soluble in alcohol, and crystallises in yellow needles having the composition  $(C_6H_4.NMe_2)_2S.C_6H_2(NO_2)_3.OH$ .

P. P. B.

**Action of Cyanogen on the Toluidines.** By J. A. BLADIN (*Bull. Soc. Chim.*, **41**, 125–130).—The author has studied the action of cyanogen on the three toluidines.

*Cyanoparatoluidine*,  $(C_7H_7.NH.CNH)_2$ , is obtained by the action of cyanogen on an alcoholic solution of paratoluidine. The crystalline product is purified by solution in sulphuric acid and precipitation with ammonia. When crystallised from alcohol, it forms nacreous scales which decompose before melting. The base combines with acids to form colourless salts, of which the *hydrochloride*, *nitrate*, *sulphate*, and *acid oxalate* are described in the original paper.

*Paratolyloxamides*.—By evaporating cyanoparatoluidine with an excess of concentrated acetic acid, *monoparatolyloxamide*,



is obtained in white needles, easily soluble in alcohol, and melting at  $236$ – $237^\circ$ . It is decomposed by the action of potash, with formation of ammonia, oxalic acid, and paratoluidine. By the reaction of acetic acid with cyanoparatoluidine, diparatolyloxamide,  $(C_7H_7.NH.CO)_2$ , is also formed. The two bodies are separated by means of boiling water, in which the latter is insoluble. It crystallises from alcohol in colourless scales which melt at  $267$ – $268^\circ$ . These crystals readily sublime when heated, and are only slowly decomposed by boiling potash. This substance has previously been studied by Wilm and Girard, who state that the melting point is  $269^\circ$ .

*Dicyanotriparatolyguanidine*,  $C_{21}H_{23}N_5$ .—This body was isolated from the liquid remaining after the crystallisation of cyanoparatoluidine. It crystallises in long yellow needles, which melt at  $182^\circ$ , and are very soluble in alcohol, insoluble in water. The body has been previously obtained by Lavdgrebe by the action of hydrochloric acid on

*dicyanodiparatolylguanidine*. It forms red and orange salts with acids. The *hydrochloride*, *platinochloride*, *sulphate*, and *nitrate* are described.

*Cyanorthotoluidine* is prepared by acting on orthotoluidine with cyanogen. It is more soluble in water than cyanoparatoluidine, and crystallises in nacreous needles. It forms salts which are easily soluble in water. The *hydrochloride*, *nitrate*, *sulphate*, and *oxalate* are described.

*Orthotolylloxamides* are obtained by methods similar to those employed in the preparation of the para-compounds. The diortho-derivative is more soluble in alcohol than the corresponding para-compound.

*Cyanometatoluidine*.—Metatoluidine, prepared by the action of zinc on nitrobenzaldehyde, is treated in alcoholic solution with cyanogen. The liquid yields rhombic crystals of cyanometatoluidine, which melt at  $200^{\circ}$ , and resemble the para- and ortho-compounds. The *hydrochloride*, *nitrate*, and *sulphate* of this base are described. The mother-liquors from the preparation of the above compound deposit small red crystals, but not in quantity sufficient to admit of examination.

*Metatolylloxamides* may be obtained by the methods described for the preparation of the corresponding para- and ortho-compounds. The mono-derivative crystallises from boiling alcohol in silvery scales melting at  $131^{\circ}$ .

The author intends to study the action of cyanogen on orthophenylene diamine and on orthamidophenol.

W. R. D.

**Action of Ethylene Bromide on Nitraniline and on Nitrotoluidine.** By L. GATTERMANN and H. HAGER (*Ber.*, 17, 778—780).—Metanitraniline is heated with ethylene bromide at  $120$ — $130^{\circ}$ , and the resulting mass treated with boiling alcohol; the red residual product, whose formula is  $(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH})_2\text{C}_2\text{H}_4$ , is best crystallised from glacial acetic acid; it melts at  $206^{\circ}$ . It forms salts only with concentrated acids, and even these are easily decomposed by water. When reduced with tin and hydrochloric acid, it is converted into *ethylene-diphenylenediamine*,  $(\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH})_2\text{C}_2\text{H}_4$ , which crystallises from its hot aqueous solution with 1 mol.  $\text{H}_2\text{O}$ ; its salts crystallise easily, and, like those of metaphenylenediamine, give a deep-brown coloration with the least trace of nitrous acid. The hydrochloride has the composition  $(\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH})_2\text{C}_2\text{H}_4 \cdot 4\text{HCl}$ .

By the action of ethylene bromide on metanitroparatoluidine, there is formed *ethyleneditoluylenenitramine*,  $(\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH})_2\text{C}_2\text{H}_4$ , crystallising from chloroform in red plates which melt at  $195^{\circ}$ . By reduction, it yields *ethyleneditoluylenediamine*,  $(\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH})_2\text{C}_2\text{H}_4$ , melting at  $158$ — $159^{\circ}$ , and crystallising from alcohol in colourless needles, which afterwards turn violet.

H. B.

**Derivatives of the Amidoethylbenzenes.** By H. PAUCKSCH (*Ber.*, 17, 767—770).—Hofmann and Benz have prepared para-amidoethylbenzene, whilst Beilstein and Kuhlberg, by nitration of ethylbenzene and reduction of the isolated products, prepared both the ortho- and para-amido-derivatives. It is, however, preferable to reduce the mixed nitro-substitution products, convert the amides into their acetyl compounds, and separate these by their solubility in

water, the para-compound separating first; it melts at  $94^{\circ}$ , whilst the ortho-compound melts at  $110$ – $112^{\circ}$ . The free bases may then be prepared, the para-compound boiling at  $213$ – $214^{\circ}$ , the ortho at  $210$ – $211^{\circ}$ . Both bases are converted into thiocarbamides,  $C_{17}H_{20}N_2S$ , by heating them with carbon bisulphide and a little alkali; these are white crystalline solids, melting at  $144$ – $145^{\circ}$  (para), and  $141$ – $142^{\circ}$  (ortho). In the preparation of the latter, some thiocarbimide is also formed; this cannot be distilled alone without alteration, but passes over in a current of steam. When heated with aniline, it yields a carbamide melting at  $148^{\circ}$ .

The paracetyl compound, treated in the cold with strong nitric acid, is converted into a dinitro-substitution product,  $C_6H_3Et(NO_2)_2.NHAc$ ; this, when heated with hydrochloric acid, yields the free base, an almost indifferent body, crystallising from alcohol in orange-yellow prisms which melt at  $134$ – $135^{\circ}$ . If, however, fuming nitric acid be dropped into a well-cooled solution of the acetyl compound in glacial acetic acid, a mononitro-derivative,  $C_6H_3Et(NO_2).NHAc$ , is obtained, very soluble in benzene, &c., and melting at  $45$ – $47^{\circ}$ . Treated with hydrochloric acid, a salt is formed, which however is easily decomposed by water with separation of the free base,  $C_6H_3Et(NO_2).NH_2$ , in small reddish-yellow crystals melting at  $45$ – $47^{\circ}$ .

H. B.

**Formanhydroisodiamidotoluene (Methenylisotoluyldiamine).** By H. HÜBNER and R. SCHÜPPHAUS (*Ber.*, **17**, 775–777).—Reference is given to a former paper (*Annalen.*, **208**, 286).

The compound,  $C_6H_3Me \begin{array}{c} \diagup N \\ \diagdown NH \end{array} CH$  [Me : NH : N = 1 : 3 : 4 or 1 : 4 : 3],

is already known, whilst that now described is [Me : NH : N = 1 : 2 : 3 or 1 : 3 : 2].

Acetorthotoluide, when treated with nitric acid, yields a product consisting principally of  $C_6H_3Me(NH_2).NO_2 = [1 : 3 : 4]$ . If it, however, be first brominated and then nitrated, the body



is obtained, which is reduced and converted into the brominated isoanhydro-base by the action of formic acid; the bromine is finally removed by sodium amalgam and water.

*Bromisoortho-diamidotoluene*,  $C_6H_2MeBr(NH_2)_2$ , melts at  $59^{\circ}$ ; its hydrochloride and sulphate are crystalline.

*Bromoformanhydroiso-diamidotoluene*,  $C_6H_2MeBr \begin{array}{c} \diagup N \\ \diagdown NH \end{array} CH$ , crys-

tallises from water in needles melting at  $187^{\circ}$ . Its salts, hydrochloride, double mercuric chloride, and platinochloride, sulphate, chromate, nitrate, and picrate, are all crystalline.

*Formanhydroiso-diamidotoluene*,  $C_6H_3Me \begin{array}{c} \diagup N \\ \diagdown NH \end{array} CH$ , is easily soluble

in water, alcohol, and benzene; it forms colourless needles melting at  $143^{\circ}$ . The platinochloride and nitrate are both crystalline.

The work is being continued.

H. B.

**Action of Monochloracetic Acid on Orthamido- and Paramido-phenol and Hydroxyphenylglycines.** By H. VATER (*J. pr. Chem.* [2], 29, 286—299).—Phenylglycine was first prepared by Michaelsen and Lippmann (*Compt. rend.*, 61, 739; *Zeitschr. f. Chem.*, 1866, 15) from monobromacetic acid and aniline, and subsequently by Schultzen, Nencki, P. J. Meyer, and Schwebel (*Abstr.*, 1878, 795), who used monochlor- instead of monobrom-acetic acid. The author has investigated the action of the latter acid on the amidophenols.

*Orth-hydroxyphenylglycine*,  $\text{HO.C}_6\text{H}_4.\text{NH.CH}_2.\text{COOH}$ , is prepared by boiling monochloracetic acid (1 mol.) with orthamidophenol (2 mols.) and 20 times the weight of water, as long as hydrochloric acid is eliminated. The hydroxyphenylglycine is separated from the more soluble hydrochloride of orthamidophenol by crystallisation. It crystallises with 1 mol.  $\text{H}_2\text{O}$  in colourless plates; it has a neutral reaction, but decomposes carbonates on heating, and forms salts both with alkalis and mineral acids. When heated at  $100^\circ$ , it loses  $2\text{H}_2\text{O}$  and forms an anhydride, which at  $143^\circ$  again loses water, but these anhydrides have not been further examined.

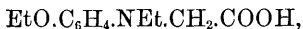
*Parahydroxyphenylglycine* is prepared in the same manner as the above, paramidophenol being employed in place of the ortho-compound. It crystallises without water in small nodules; even at  $200^\circ$ , it suffers no change. A solution in hydrochloric acid gives a dark violet and then a yellow coloration with chloride of lime. It has a neutral reaction and forms salts with acids and bases, but the hydrogen of the hydroxyphenyl-group is not replaceable by metals.

*Orthmethoxyphenylglycine*,  $\text{MeO.C}_6\text{H}_4.\text{NH.CH}_2.\text{COOH}$ , is prepared in the same way as the above by heating monochloracetic acid and orthanisidine with water, and then shaking with ether; the glycine dissolves and can be purified by recrystallisation from ether, when it is obtained in rectangular plates, which melt at  $141.5^\circ$ ; it forms salts like the above-mentioned compounds.

*Paramethoxyphenylglycine* was prepared from paranisidine in a similar manner. It decomposes at  $200^\circ$  without melting. The two methoxyphenylglycines are isomeric with tyrosine.

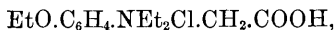
*Orthethoxyphenylglycine*,  $\text{EtO.C}_6\text{H}_4.\text{NH.CH}_2.\text{COOH}$ , prepared from orthamidophenetoil, melts at  $120^\circ$ .

*Ethylic orthethoxyphenylglycinate*,  $\text{EtO.C}_6\text{H}_4.\text{NH.CH}_2.\text{COOEt}$ , is prepared by acting with ethylic monochloracetate on orthamidophenetoil in alcoholic solution. *Orthethoxyphenylethylglycine*,



obtained by acting with monochloracetic acid on orthomonethyl-amidophenetoil in alcoholic solution, is isomeric with this compound.

*Orthethoxyphenyldiethylglycinic chloride*,



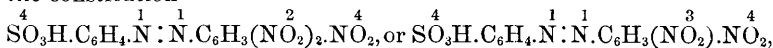
is prepared by heating in a sealed tube at  $100^\circ$  a mixture of equal molecular weights of monochloracetic acid and orthodiethylamidophenetoil dissolved in its own volume of ether. The chloride was only obtained as a syrup, but the platinochloride was prepared. The chloride is decomposed by soda with formation of a neutral oil inso-

luble in water, but soluble in alcohol and ether; in all probability this was the hydroxide. It is soluble in acids, but not in caustic alkalis, showing that the acid properties of the oxyphenylglycine have disappeared. P. F. F.

**Amidocresols.** By A. MAARSEN (*Ber.*, **17**, 608—610).—Wallach has shown (*Abstr.*, 1883, 329) that when *metatoluylenediamine* is converted into the acetic compound, the acetoxyl group takes up the para-position, and from this an amidocresol, melting at 159—161°, is obtained, different from that obtained from nitrotoluidine,  $C_6H_3Me(NO_2).NH_2$  [1 : 2 : 4]. The amidocresol obtained from this nitrotoluidine has been converted into the acetic derivative by heating it with acetic anhydride. It melts at 178°, whereas the monacetamidocresol obtained by Wallach from *metatoluylenediamine* melts at 224—225°, so that the two amidocresols are isomeric. A further confirmation of this is to be found in the fact that Nölting and Collin (this vol., p. 1087) have obtained from nitro-orthotoluidine an amidocresol,  $C_6H_3Me(OH).NH_2$  [1 : 2 : 4], identical with that prepared by Wallach. P. P. B.

**Substitution-products of Azobenzene and an Unsymmetrical Triamidobenzene.** By J. V. JANOVSKY (*Monatsh. Chem.* **5**, 155—164).—In the author's paper on the nitro-derivatives of azobenzene-parasulphonic acid (*Abstr.*, 1883, 324), he described two mononitro-acids and a dinitro-acid. The position of the nitro-groups in the mononitro-acids was subsequently determined (*Abstr.*, 1883, 1101), but in the case of the dinitro-acid the possible isomerides are so numerous that a determination of the positions of the nitro-groups seemed impossible, and it appeared best to take one of the mononitro-acids and prepare a dinitro-acid from that. For this purpose para-nitroazobenzeneparasulphonic acid was heated with  $4\frac{1}{2}$  times the quantity of nitric acid of sp. gr. 1·48—1·5; on addition of water the whole solidifies to a crystalline magma, from which the dinitro-acid is obtained on recrystallisation.

*Dinitroazobenzeneparasulphonic acid*,  $C_{12}H_7(NO_2)_2N_2.SO_3H$ , crystallises sometimes in rounded needles, sometimes in rosettes. Most of the salts are very sparingly soluble in water. The potassium salt,  $C_{12}H_7(NO_2)_2N_2.SO_3K + aq$ , is obtained as a yellow precipitate of microscopic needles; the sodium salt crystallises in microscopic flat needles, is readily soluble in hot water, sparingly soluble in cold water; the barium salt,  $[C_{12}H_7(NO_2)_2N_2.SO_3]_2Ba$ , is obtained as a yellow microcrystalline precipitate. By moderated reduction, the dinitro-acid yields a deep yellow-coloured product, now under investigation: on complete reduction, it yields sulphanilic acid and unsymmetrical triamidobenzene. With regard to the constitution of the dinitro-acid, its reduction-products show that it must have the constitution



as it appears to be identical with the acid obtained by the direct nitration of azobenzeneparasulphonic acid, which must be regarded



as formed by the further nitration of both the para- and metamonitro-acids; the latter formula is the most probable.

*Unsymmetrical triamidobenzene*,  $C_6H_3(NH_2)_3$  [1:2:4], prepared as above mentioned by the reduction of the dinitro-acid with tin and hydrochloric acid, forms a white crystalline mass which readily becomes discoloured. It melts at 132–133°, and gives an emerald-green coloration with oxidising agents, such as ferric chloride and potassium chromate. The hydrochloride crystallises in long colourless needles, becoming brownish-red on exposure to air. Oxidising agents colour it first violet, then green. The platinochloride forms a crystalline yellow powder. This triamidobenzene must be identical with that obtained from chrysoidine (this Journal, 1877, ii, 458); it is distinguished from the symmetrical triamidobenzene by its melting point and colour reaction.

*Parabromazobenzeneparasulphonic acid*,  $SO_3H.C_6H_4.N^1:N^1.C_6H_4Br^4$ , is prepared by treating the parasulphonic acid under water with bromine. It crystallises in fine needles, and is a strong acid, displacing hydrochloric and nitric acid from their alkali salts in the cold. Its salts crystallise well, are readily soluble in hot, sparingly in cold water. The potassium salt,  $C_{12}H_8BrN_2.SO_3K$ , is obtained as an orange-yellow silky precipitate. On recrystallisation, it yields well-formed plates. The sodium salt crystallises in orange-yellow needles. The barium and calcium salts crystallise in groups of fine needles, very sparingly soluble even in hot water. The zinc salt crystallises in plates. On reduction with tin and hydrochloric acid, the free acid yields sulphanilic acid and parabromamidobenzene.

A. J. G.

**Azo-compounds.** By C. LIEBERMANN and S. v. KOSTANECKI (*Ber.*, 17, 876–887; see Abstr., 1883, 736, and *Ber.*, 16, 2358).—The same results were obtained in the reduction by tin and hydrochloric acid of phenylazoparacresol and phenylazo-orthocresol as were obtained by Nölting and Kohn (this vol., 900).

By the action of diazobenzene on the phenols, not only are colouring matters soluble in potash formed, but others insoluble in alkalis, and belonging to a different class of compounds. By allowing the aniline hydrochloride and acidified potassium nitrite solutions to react for a sufficient length of time before adding the alkaline solution of the phenol, only those colours soluble in potash are formed. If, however, the phenol solution be quickly added after mixing the amido-salt and the nitrous acid, there are formed nitrosophenols, which afterwards react with the amido-base to form diazo-compounds, which may have a different constitution to those formed by the former method. During the preparation of phenylazoparacresol, azo-orthocresol, and phenylazophenol, these bye-products, insoluble in alkalis, are formed in large quantity. After complete purification, they proved to be diazoamidobenzene in each instance.

By the action of diazobenzene hydrochloride on resorcinol, two colouring matters are obtained, one—phenylazoresorcinol—easily soluble in dilute alkalis; the other only sparingly soluble, and insoluble in alcohol. This last substance has been examined previously, but not

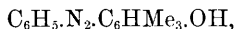
with success; it is *phenyldisazoresorcinol*,  $(C_6H_5.N_2)_2C_6H_2(OH)_2$ , and crystallises in red needles melting at  $220-222^\circ$ . Its acetyl derivative,  $(C_6H_5.N_2)_2C_6H_2(OAc)_2$ , forms yellow needles melting at  $137-138^\circ$ . The constitution of phenyldisazoresorcinol is proved by the action of tin and hydrochloric acid, aniline and diamidoresorcinol being formed. There are four possible phenyldisazoresorcinols; two have been described by Wallach; the above is a third; its constitution is partly indicated by the identity of the diamidoresorcinol obtained with that prepared by Fitz from dinitroresorcinol.

Amidopseudocumene (melting at  $62^\circ$ ), when heated with potassium nitrite and resorcinol, yields two products, one soluble in alkalis—*cumylazoresorcinol*,  $C_6H_2Me_3.N_2.C_6H_3(OH)_2$ , melting at  $199^\circ$ —the other insoluble in alkalis—*cumyldisazoresorcinol*,  $(C_6H_2Me_3.N_2)_2C_6H_2(OH)_2$ , forming red needles. Similar bodies obtained from liquid cumidine boiling at  $225-231^\circ$ , have been described.

Employing paramidophenetoil and resorcinol, only one product, that soluble in alkalis, was formed, namely, *paraphenetoilazoresorcinol*, crystallising in red plates which melt at  $165-167^\circ$ .

The authors had intended to introduce into paracresol a series of different diazo-residues, and afterwards to examine other para-substituted phenols in the same manner. Nölting and Kohn having experimented in the first direction, the authors only describe the action of diazoparaphenetoil on paracresol. There is formed only *paraphenetoilazoparacresol*,  $EtO.C_6H_4.N_2.C_6H_3Me.OH$ ; it is only moderately soluble in alkalis, and forms golden scales which melt at  $103-104^\circ$ ; by reduction with tin and hydrochloric acid, it yields paramidophenetoil and amidoparacresol.

Among the other para-substituted phenols examined were parachlorophenol, parazophenol, and paranitrophenol; the last did not enter into reaction at all with diazocumene, the second did so, but the product could not be purified. On the other hand, the cumenol obtained from the solid cumidine easily enters into reaction; thus with diazocumene, it yields *cumylazocumenol*,  $C_6H_2Me_3.N_2.C_6HMe_3.OH$ , remarkable for its complete insolubility in alkalis—resembling thus the corresponding compounds of  $\beta$ -naphthol—it is, however, soluble in alcohol and melts at  $147-148^\circ$ . *Phenylazocumenol*,

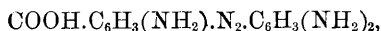


crystallises in brown prisms melting at  $93-94^\circ$ ; on reduction, it yields aniline and *hydroxycumidine*,  $HO.C_6HMe_3.NH_2$ , subliming in white needles which melt at  $166-167^\circ$ ; this base does not yield any quinone when treated with chromic acid, and when treated with acetic anhydride it does not yield an anhydride, but *acetoxycumylcumidine*,  $AcO.C_6HMe_3.NHAc$ . *Potassium-sulphanilazocumenol*,  $KSO_3.C_6H_4.N_2.C_6HMe_3.OH + 2H_2O$ , forms orange needles, and on reduction yields sulphanilic acid and amidocumenol. H. B.

**Metazo- and Hydrazo-phenetoil.** By M. BUCHSTAB (*J. pr. Chem.* [2], 29, 299–300).—This is a preliminary note on the formation of these bodies by the reduction of metanitrophenetoil.

By the action of sodium amalgam on this in alcoholic solution, met-azophenetoil is formed; it is soluble in alcohol and ether, but insoluble in water, and crystallises in orange-yellow prisms which melt at  $91^{\circ}$ . By passing sulphuretted hydrogen through an alcoholic solution of the metazophenetoil, and adding water, metahydrazophenetoil separates; it crystallises in colourless needles which melt at  $91^{\circ}$ . The hydrazophenetoil is converted into the corresponding diethoxybenzidine by treatment with mineral acids. P. F. F.

**Diazo-derivatives.** By P. GRIESS (*Ber.*, **17**, 603—608).—When Paramidobenzoic acid is treated with nitrous acid, it yields a compound isomeric with  $\beta$ - and  $\gamma$ -azimidobenzoic acids, which the author styles *paramidodiazobenzoic acid*. It crystallises from hot water in yellow needles or narrow four-sided plates, containing 3 mols.  $\text{H}_2\text{O}$ , which it loses at  $100^{\circ}$ . This compound does not exhibit the characters of an acid, and to it the author assigns the constitution  $\text{NH}_2\cdot\text{C}_6\text{H}_3\langle\text{N}:\text{N}\rangle\text{CO}$ . It possesses basic properties and forms a hydrochloride,  $(\text{C}_7\text{H}_5\text{N}_3\text{O}_2)_2\cdot\text{HCl}$ , which crystallises in white six-sided plates; its *platinochloride*,  $(\text{C}_7\text{H}_5\text{N}_3\text{O}_2)_2\cdot\text{H}_2\text{PtCl}_6$ , is sparingly soluble in water and crystallises in small yellow rhombic leaflets. The *aurochloride*,  $(\text{C}_7\text{H}_5\text{N}_3\text{O}_2)_2\cdot\text{HAuCl}_4$ , forms dark-yellow insoluble needles. It forms a perbromide which has not been analysed. This paramidodiazobenzoic acid is a true diazo-compound, uniting directly with aromatic amines and phenols to form azo-compounds. Thus with *metaphenylenediamine* it forms a compound,



and with  $\beta$ -*naphthol* the compound  $\text{COOH}\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ . The three phenylenediamines behave with nitrous acid in a similar manner to the three diamidobenzoic acids. Ladenburg has already shown (this vol., 739) that *orthophenylenediamine* yields *azimidobenzene*; *metaphenylenediamine* forms *triamidoazobenzene* (phenylene brown), whilst the para-compound forms a compound similar to the above-mentioned *paramidodiazobenzoic acid*, which the author styles *amido-diazobenzene*. The free base is very unstable, but its salts are stable compounds; the *aurochloride*, which has the composition



is insoluble in water, and from it the salts are best prepared.

The compound,  $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$ , obtained by Ladenburg by the action of nitrous acid on *paraphenylenediamine*, the author considers to be a product of the decomposition of amidoazobenzene. P. P. B.

**Derivatives of Amidoazobenzene.** By G. BERJU (*Ber.*, **17**, 1400—1406).—*Acetyl-amidoazobenzene*,  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , prepared by treatment of amidoazobenzene with acetic anhydride, crystallises in slender yellow needles, melts at  $143^{\circ}$ , and does not unite with acids to form salts. A. Muller has previously given some account of this substance and of its conversion into *acetylhydrazobenzene*.

*Monomethylamidoazobenzene*,  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}$ , is prepared by heating amidoazobenzene and methyl iodide for two hours at  $50^\circ$  in a reflux apparatus. It crystallises in brick-red needles, melts at  $180^\circ$ , is soluble in alcohol, and reprecipitated on adding water. The hydrochloride forms violet needles. When treated with acetic anhydride, it yields *acetylmonomethylamidoazobenzene*,  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMeAc}$ , crystallising in silky yellow needles melting at  $139^\circ$ .

*Dimethylamidoazobenzene*,  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , prepared by Griess (this Journal, 1877, ii, 456), by the action of diazobenzene on dimethylaniline, can also be obtained by the action of methyl iodide on monomethylamidoazobenzene.

*Trimethylazobenzeneammonium iodide*,  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I}$ , prepared by the action of methyl iodide on the dimethyl compound in sealed tubes at  $100^\circ$ , crystallises in flesh-coloured plates, melts at  $173\text{--}174^\circ$ , and is soluble in alcohol and hot water. It is not decomposed by boiling with alkalis.

*Benzylidenamidoazobenzene*,  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{CHPh}$ , is prepared by the action of benzaldehyde on amidoazobenzene in the cold. It crystallises in orange-coloured plates, is soluble in dilute alcohol, and is resolved into benzaldehyde and amidoazobenzene hydrochloride on treatment with hydrochloric acid.

*Dibromamidoazobenzene*,  $\text{C}_{12}\text{H}_9\text{N}_3\text{Br}_2$ , prepared by the action of an alcoholic solution of bromine on amidoazobenzene, crystallises in bright yellow needles and melts at  $152^\circ$ . By the action of tin and hydrochloric acid, it is converted into aniline and paraphenylenediamine.

*Carbamidoazobenzene*,  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph})_2$ , is obtained, together with amidoazobenzene hydrochloride, by the action of carbon oxychloride on amidoazobenzene, both dissolved in benzene. It crystallises in microscopic plates, melts with decomposition at  $270^\circ$ , is sparingly soluble in alcohol, more readily soluble in chloroform and benzene.

By boiling alcoholic solutions of amidoazobenzene and phenyl thiocarbimide, a yellow mass is obtained from which on treatment with alcohol *azobenzenemonophenylthiocarbamide*,



can be dissolved out and crystallises on cooling in microscopic plates melting at  $179^\circ$ . The portion insoluble in alcohol consists of *thiocarbamidazobenzene*,  $\text{CS}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph})_2$ ; it melts at  $199^\circ$ , and is converted into carbamidazobenzene by treatment with yellow mercuric oxide.

A. J. G.

**Helianthin.** By R. MÖHLAU (*Ber.*, 17, 1490—1493).—If nitrous acid is passed into a solution of equivalent proportions of the hydrochlorides of aniline and dimethylaniline, diazobenzene chloride and nitrosodimethylaniline are formed. If, however, an alkaline sodium nitrite solution is used in place of nitrous acid, *dimethylamidoazobenzene*,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}$ , is formed. It is best to mix a solution of 7.4 grams sodium nitrite and 4 of sodium hydroxide in 54 c.c. water with a solution of 10 grams aniline, 13 of dimethylaniline, and 23 c.c. hydrochloric acid (sp. gr. 1.171 at  $15^\circ$ ), in 36 c.c. of water.

The mixture should be kept agitated and the temperature not allowed to exceed 15°. The substance has already been described by Griess (this Journal, 1877, ii, 456). If 1 part of this substance is dissolved in 20 parts of sulphuric acid which contains 30 per cent. anhydride, and allowed to stand for about 24 hours, a very satisfactory yield of its sulphonic acid (also described by Griess, *loc. cit.*) is obtained. This forms a convenient method for the preparation of helianthin (or Orange III) of commerce, which is the sodium or ammonium salt of dimethylamidoazobenzenesulphonic acid.

When orthotoluidine is substituted for aniline in the foregoing reaction, the results are not satisfactory, but if paratoluidine is used, *dimethylamidobenzeneazotoluene*,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{Me}$ , is formed. It crystallises in golden-yellow scales, soluble in alcohol and ether; it melts at 168—168·5°, and distils with scarcely any decomposition. The chloride and sulphate crystallise in violet prisms which yield a magenta-coloured solution with alcohol. On reduction, it yields paratoluidine and dimethylparaphenyldiamine. No sulphonic acid could be obtained directly, but *dimethylamidobenzeneazotoluenesulphonic acid*,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{SO}_3\text{H}$  [ $\text{Me} : \text{SO}_3\text{H} : \text{N} = 1 : 3 : 4$ ], was obtained by Griess's method by acting on diazoparatoluidine-sulphonic acid with dimethylaniline. It crystallises in very dark violet prisms, soluble to an orange solution in alcohol and in hot water, but insoluble in ether. The sodium salt crystallises in glittering orange scales.

L. T. T.

### Phenylhydrazine, a Reagent for Aldehydes and Ketones.

By E. FISCHER (*Ber.*, **17**, 572—578).—In a former communication (*Ber.*, **16**, 661) the author pointed out the utility of this reagent in detecting the presence of aldehydes, &c.; further investigation shows that it may also be used to identify aldehydes, ketones, and ketonic acids. The method adopted in using this reagent is first to prepare phenylhydrazine hydrochloride by neutralising the base dissolved in 10 parts of alcohol with hydrochloric acid, the crystalline hydrochloride is filtered off, washed with alcohol and ether, and dried. One part by weight of the hydrochloride is added to one and a-half times its weight of sodic acetate dissolved in 8—10 parts by weight of water; the reagent so prepared is added to the aqueous solution of the aldehyde, &c., with which in the majority of cases it reacts directly, in some cases heating on the water-bath is required to bring about the desired reaction. Free mineral acids interfere with the reaction, and require to be neutralised, the presence of nitrous acid is specially injurious, and is most easily removed by treatment with carbamide.

With this reagent, acetic, propionic, butyric, valeric, and cœnanthylic aldehydes yield colourless non-crystallisable oils.

Furfuraldehyde in aqueous solutions yields a yellowish oil, which solidifies after a short time; from its ethereal solution, the compound is precipitated by petroleum in colourless plates, melting at 97—98°; the compound has the formula  $\text{N}_2\text{HPh} : \text{C}_5\text{H}_4\text{O}$ . One part of furfuraldehyde dissolved in 10,000 parts of water gives a precipitate with a

solution of hydrazine in 15 minutes, and 1 part in 1000 produces an immediate precipitate.

With *benzaldehyde*, the reagent yields a precipitate of the compound  $N_2HPh : CHPh$ , melting at  $152.5^\circ$ . An aqueous solution of benzaldehyde of 1 in 2000 gives first a turbidity, which on shaking forms a white flocculent precipitate, and the reaction takes place even with a solution of 1 in 50,000.

*Cinnamic aldehyde* suspended in water unites with the phenylhydrazine immediately if the solution is warmed, forming a white crystalline solution of the compound  $N_2HPh : CH.C_2H_2Ph$ ; this crystallises from alcohol in fine yellow needles or plates melting at  $168^\circ$ .

*Salicylaldehyde*, *cuminaldehyde*, *anisaldehyde*, and *para-hydroxybenzaldehyde*, all form crystalline hydrazine-derivatives. The reagent yields an immediate precipitate with a slightly warmed aqueous solution of *glyoxal*; the compound formed is insoluble in alkalis and dilute acids, and crystallises from alcohol in fine leaflets, melting at  $169-170^\circ$ , having the composition  $N_2HPh : CH.CH : N_2HPh$ .

The reagent produces insoluble liquid condensation-products with aqueous solutions of the ketones, which on being heated with acids are easily resolved into hydrazine and the ketone.

*Acetophenone* suspended in water gives a yellow crystalline mass, crystallising from alcohol in fine scales melting at  $105^\circ$ .

*Benzylideneacetone*, when warmed with an excess of the reagent, gives a solid which crystallises from hot alcohol in yellow prismatic plates, of the formula  $CHPh : CH.CMe : N_2HPh$ , and melting at  $175^\circ$ .

*Benzophenone* yields the compound  $N_2HPh : CPh_2$ , which is insoluble in dilute alcohol, but soluble in hot alcohol, from which it crystallises in colourless needles melting at  $137^\circ$ .

*Isatin* also unites with phenylhydrazine, 1 part in 2000 parts of water yielding a heavy precipitate of fine yellow needles on boiling; the reaction takes place even with a solution of 1 in 20,000. The compound formed has the composition  $C_{14}H_{11}N_3O$ , and crystallises from alcohol in fine yellowish-red needles melting at  $210-211^\circ$ .

Phenylhydrazine unites also with ketonic and aldehyde acids, the union taking place in hydrochloric or acetic acid solutions. The compounds are sparingly soluble in water, and separate out as yellow crystalline precipitates.

*Phenylhydrazineglyoxylic acid*,  $N_2HPh : CH.COOH$ , crystallises from alcohol or water in fine yellow needles which decompose at  $137^\circ$ . It is soluble in caustic alkalis, and acids precipitate it unaltered from the solutions.

*Phenylhydrazinepyrrocemic acid*,  $N_2HPh : CMe.COOH$ , crystallises from alcohol in fine prisms which melt at  $192^\circ$ ; the reaction will show the presence of 1 part of pyrrocemic acid in 1000 of water.

*Phenylhydrazinemesoxylic acid*,  $N_2HPh : C(COOH)_2$ , crystallises from hot water or dilute alcohol in fine yellow needles melting at  $163-164^\circ$ .

Phenylglyoxylic acid unites with phenylhydrazine, forming a compound which crystallises from hot acetic acid in fine yellow needles melting at  $153^\circ$ , and having the composition  $N_2HPh : CPh.COOH$ .

P. P. B.

**Action of Phenylhydrazine on Cyanhydrins.** By A. REISSERT (*Ber.*, 17, 1451—1462).—In continuation of the researches of Tiemann, Piest, and Stephan (*Abstr.*, 1883, 198, *et seq.*) on the action of aniline on many of the cyanhydrins (hydroxynitriles), the author has investigated the action of hydrazine on the cyanhydrins of benzaldehyde, acetaldehyde, and acetone.

Benzaldehyde cyanhydrin acts on phenylhydrazine in alcoholic solution with development of heat, benzylidenephénylhydrazine,  $\text{CHPh:N}_2\text{HPh}$ , being formed. It melts at  $152.5^\circ$ , and has been described by E. Fischer (*Abstr.*, 1878, 309). The same compound is produced if the aldehyde is replaced by phenylchloroacetic acid. Neither nitrile nor hydrazido-acid could be obtained.

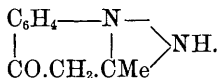
$\alpha$ -Phenylhydrazidopropionitrile,  $\text{PhN}_2\text{H}_2\cdot\text{CHMe}\cdot\text{CN}$ , is obtained by acting on acetaldehyde cyanhydrin with phenylhydrazine in alcoholic solution. It forms crystals which melt at  $58^\circ$ , and dissolve readily in alcohol and ether, sparingly in benzene and cold light petroleum. When heated with mineral acids or alkalis, it decomposes into hydrocyanic acid and ethylidene-phenylhydrazine, and this latter, by further action of acids, yields acetaldehyde and phenylhydrazine. When it is dissolved in fuming hydrochloric acid and after remaining at rest for several days is neutralised with ammonia, it yields  $\alpha$ -phenylhydrazidopropionamide,  $\text{PhN}_2\text{H}_2\cdot\text{CHMe}\cdot\text{CONH}_2$ . This substance forms hard white crystals which melt at  $124^\circ$ , are easily soluble in alcohol and boiling water, more sparingly in ether, and almost insoluble in benzene, chloroform, and light petroleum. With acids, it forms salts which decompose Fehling's solution on boiling. When boiled with alkalis for some time, the amide is converted into  $\alpha$ -phenylhydrazidopropionic acid, which crystallises in glittering white needles, easily soluble in alcohol, benzene, and ether, and melting at  $187^\circ$ . It dissolves in boiling water, the solution having an acid reaction towards litmus-paper. Its barium and zinc salts are crystalline, its calcium salt amorphous. When a solution of the nitrile in excess of alcohol is saturated with hydrochloric acid, the hydrochloride of ethyl  $\alpha$ -phenylhydrazidopropionate crystallises out, and ammonia precipitates the ether from a solution of its chloride. The ethyl salt crystallises in needles which melt at  $116^\circ$ , and are easily soluble in alcohol, benzene, chloroform, and light petroleum, almost insoluble in water. Both the ether and amide yield  $\alpha$ -anilidopropionic acid and ammonia on reduction with tin and hydrochloric acid. These compounds must therefore be unsymmetrical hydrazines, and the formula of the acid be  $\text{NH}_2\cdot\text{NPh}\cdot\text{CHMe}\cdot\text{COOH}$ . The author believes the  $\alpha$ -phenylhydrazidopropionic acid described by E. Fischer and F. Jourdan to be the symmetrical body of the formula  $\text{NHPh}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{COOH}$ .

$\alpha$ -Phenylhydrazidoisobutyronitrile,  $\text{PhN}_2\text{H}_2\cdot\text{CMe}_2\cdot\text{CN}$ , is prepared from acetone in like manner to the propionitrile from acetaldehyde, except that an excess of the acetone cyanhydrin should be used. It crystallises from light petroleum in white needles which melt at  $70^\circ$ , and are easily soluble in alcohol, ether, benzene, and chloroform, insoluble in water. The amide could not be obtained—as in the case of the propionitrile—by saponification with strong hydrochloric or sulphuric acid, but in both cases an internal anhydride of the correspond-

ing butyric acid was formed.  $\alpha$ -Phenylhydrazido-isobutyric anhydride,  $\text{CMe}_2\langle\text{CO-NPh}\rangle\text{NH}$ , thus obtained is easily soluble in alcohol, benzene, ether, and chloroform, sparingly in light petroleum and water, and forms white crystals which melt at  $175^\circ$ . It forms salts with mineral acids—its hydrochloride containing 1 mol. acid to 1 mol. anhydride—and is slowly converted by boiling with sodium hydroxide into sodium  $\alpha$ -phenylhydrazido-isobutyrate,  $\text{PhN}_2\text{H}_2\cdot\text{CMe}_2\cdot\text{COONa}$ . On attempting to liberate the acid, the anhydride is at once re-formed. If, in the preparation of the anhydride by the action of strong sulphuric acid on the nitrile, the reaction is stopped *immediately* that a test portion no longer yields hydrocyanic acid on boiling with sodium hydroxide, a small quantity of  $\alpha$ -phenylhydrazido-isobutyrimide,  $(\text{PhN}_2\text{H}_2\cdot\text{CMe}_2\cdot\text{CO})_2\text{NH}$ , is formed. This body is easily prepared if a solution of the nitrile in excess of absolute alcohol is saturated with hydrochloric acid gas and the product partly evaporated on the water-bath; ammonium chloride soon separates out, and a solution of the hydrochloride of the imide is left, from which the free imide is precipitated by ammonia. It is a crystalline substance, easily soluble in alcohol, ether, benzene, and chloroform, sparingly in light petroleum and water, and melts at  $117^\circ$ . It is easily soluble in mineral acids, and with hydrochloric acid yields a white crystalline hydrochloride containing 3 mols. of acid to 1 of the base. When heated with alkalis, it yields the internal anhydride described above. Like the propio-compounds, the butyro-compounds proved to be unsymmetric hydrazines.

L. T. T.

**Action of Ethyl Acetoacetate on Hydrazine-quinizine Derivatives.** By L. KNORR (*Ber.*, **17**, 546—552).—In a former communication, the author described a compound,  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}$ , obtained by the action of phenylhydrazine on ethyl acetoacetate, which is styled *oxymethylquinizine*, having probably the constitution



Its formation takes place in two stages, first *ethylphenylhydrazine acetoacetate*,  $\text{N}_2\text{HPh}:\text{CMe}\cdot\text{CH}_2\cdot\text{COOEt}$ , is produced, which, when heated, is resolved into alcohol and oxymethylquinizine.

With nitrous acid, oxymethylquinizine yields a brown-coloured strongly acid body; with nitric acid, a nitro-compound, and a blue colouring matter, soluble in ether; and colouring matters with benzaldehyde, phthalic anhydride, &c. The hydrogen in it can be replaced by alkyl and acid radicles; for instance, *dimethyloxyquinizine* is formed when it is heated with methyl alcohol and methyl iodide in sealed tubes at  $100^\circ$ ; this compound forms beautiful needles melting at  $113^\circ$ . Its dilute aqueous solutions give a characteristic bluish-green coloration with nitrous acid, and in concentrated solutions a green crystalline precipitate, a reaction characteristic for all quinizines.

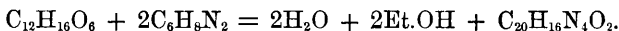
*Orthotolu-oxymethylquinizine*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}$ , obtained from orthotolylhydrazine, melts at  $183^\circ$ . It forms an *orthotolu-dimethyloxyquinizine* melting at  $96\text{--}97^\circ$ .



*Ethyl paratolylhydrazine acetoacetate*,  $C_{12}H_{18}N_2O_2$ , the product of the direct action of paratolylhydrazine on ethyl acetoacetate, forms well-defined crystals melting at  $91-93^\circ$ . Heated at  $130-140^\circ$ , it yields *paratolumethyloxyquinizine* melting at  $140^\circ$ ; its methyl derivative melts at  $137^\circ$ .

$\beta$ -*Naphtho-oxymethylquinizine*,  $C_{14}H_{10}N_2O$ , is a crystalline compound melting at  $190^\circ$ ; its methyl compound, obtained like dimethyloxyquinizine, melts at  $129^\circ$ , and is decomposed by heat.  $\alpha$ -*Naphthylhydrazine* forms similar compounds.

Phenylhydrazine and ethyl succinosuccinate yield a compound resembling methyloxyquinizine. It has the composition  $C_{20}H_{16}N_4O_2$ , is insoluble in ordinary solvents, dissolves in alkalis, forming a purple solution, from which a blue colouring matter separates out on standing. When heated, a portion carbonises, and at the same time purple vapours are formed, and a blue sublimate. The formation of this compound, which is explained by the following equation, makes it probable that all acids analogous to acetoacetic acid will react with hydrazines:—

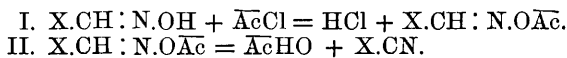


P. P. B.

**Aldoximes.** By B. LACH (*Ber.*, **17**, 1571—1575).—Gabriel (*Abstr.*, 1883, 188) has shown that nitrobenzaloxime is decomposed by the action of acetic anhydride, yielding nitrobenzonitrile, whilst according to Westernberger (this vol., 581) terephthalaldoxime forms an acetyl derivative. The author has investigated the action of acetic chloride and anhydride on aldoximes, in order, if possible, to find the characteristics which determine in which of these two ways an aldoxime shall be acted on. Both reagents behave alike, the only difference being that acetic chloride is more violent in its action.

*Benzaldoxime* yields benzonitrile. *Salicylaldoxime* yields salicylonitrile acetate,  $C_6H_4(CN).O\bar{A}c[\bar{A}cO : CN = 1 : 2]$ . *Parahydroxybenzaloxime* yields  $C_6H_4(CN).O\bar{A}c[\bar{A}cO : CN = 1 : 4]$ , which crystallises in white needles melting at  $57^\circ$ , and boiling at  $265-266^\circ$ . *Enanthaldoxime* yields enanthonitrile boiling at  $175-177^\circ$ . *Glyoxime*,  $NOH : CH.CH : NOH$ , evolves cyanogen, but crystals of diacetylglyoxime,  $NO\bar{A}c : CH.CH : NO\bar{A}c$ , were left in the flask. These crystals decompose on further heating with acetic anhydride, evolving cyanogen gas.

It thus appears that in by far the largest number of cases aldoximes are converted into nitriles by the action of acetic anhydride or chloride, and that the formation of acetyl derivatives is an intermediate stage of the reaction, which would then take place according to the equations—



L. T. T.

**Trimethylene-derivatives.** By W. H. PERKIN, jun. (*Ber.*, **17**, 1440—1444). Acetyltrimethylenecarboxylic acid (this vol., 64) is heated in portions of 5 grams for some time on an oil-bath at  $200^\circ$ ; carbonic anhydride is copiously evolved, a colourless liquid distils, and

a considerable quantity of a thick dark-coloured oil remains in the retort. On fractioning the distillate, about one-third passes over between 100—125°, and from this, after repeated distillations, *acetyl-*

*trimethylene*,  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} \text{CHAc}$ , can be isolated as a colourless mobile oil of

agreeable acetyltetramethylene-like odour. It boils at 112—113° (at 720 mm.), and is readily polymerised, especially by mineral acids, oils of high boiling point being formed. With hydroxylamine, it yields a small quantity of a derivative crystallising in needles; the greater part is polymerised.

*Benzoyltrimethylenoxime*,  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} \text{CH.CPh(NO)}$ , is prepared by

allowing a mixture of benzoylmethylene with excess of hydroxylamine solution and some alcohol to remain for some days and then extracting the product with ether. It crystallises in peculiarly striated plates, melts at 86—87°, is readily soluble in ether, benzene, chloroform, alcohol, and carbon bisulphide, sparingly in light petroleum.

By heating a mixture of benzoyltrimethylene, hydroxylamine, alcohol, and a few drops of hydrochloric acid, the reaction takes quite a different course, there being formed, according to the amount of hydroxylamine employed, either the hydrochloride of an uncrystallisable base whose isolation could not be effected, or the hydrochlorides of two bases that can be separated by the difference of their solubilities in ether and whose investigation is being continued.

To ascertain if this method of formation of trimethylene-derivatives was general or merely restricted to the action of ethylene bromide on ethyl sodacetoacetates, &c., the action of propylene bromide on ethyl sodacetoacetate was investigated. The product of the reaction is

*ethylic acetylmethyltrimethylenecarboxylate*,  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CHMe} \end{array} \text{CAc.CO}^-\text{OEt}$ ; it is a colourless liquid of feeble odour, boils at 210—215° (720 mm.) and is isomeric with ethyl acetyltetramethylenecarboxylate (b. p. 225°).

*Acetylmethyltrimethylenecarboxylic acid*,  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CHMe} \end{array} \text{CAc.COOH}$ , is prepared from the ethyl salt, by heating it for four hours on the water-bath with alcoholic potash, neutralising with sulphuric acid, evaporating to dryness, acidulating with sulphuric acid, and extracting with ether. It forms a nearly colourless thick oil, is moderately stable towards alkalis, but is readily decomposed with evolution of carbonic anhydride when heated with acids. Heated alone, it yields carbonic anhydride and a colourless mobile liquid probably acetylmethyltrimethylene. The silver salt,  $\text{C}_7\text{H}_9\text{O}_3\text{Ag}$ , is obtained as an amorphous white powder.

A. J. G.

**Diphenylacetoxime.** By E. SPIEGLER (*Monatsh. Chem.*, 5, 203—207). Diphenylacetoxime was prepared by Janny (*Abstr.*, 1883, 4 i 2

580), the present paper deals with some of its derivatives. The methyl, ethyl and benzyl ethers may be prepared by adding to an alcoholic solution of diphenylacetoxime somewhat less than the calculated amount of sodium alcoholate and a slight excess of the halogen-compound of the radical required. The mixture is then heated for several hours in a reflux apparatus, the alcohol evaporated off on the water-bath, water and a few drops of soda added, and the liquid extracted with ether.

*Diphenylacetoxime methyl ether*,  $\text{CPh}_2\text{NOMe}$ , is obtained in pale yellow crystals melting at  $92^\circ$ .

*Diphenylacetoxime ethyl ether*,  $\text{CPh}_2\text{NOEt}$ , forms a yellow oil of sharp bitter taste and unpleasant odour; it boils with partial decomposition at  $276-279^\circ$ .

*Diphenylacetoxime benzyl ether*,  $\text{CPh}_2\text{NO}\cdot\text{CH}_2\text{Ph}$ , is obtained in white crystals melting at  $55-56^\circ$ .

*Acetyl-diphenylacetoxime*,  $\text{CPh}_2\text{NO}\overline{\text{Ac}}$ , is prepared by heating diphenylacetoxime with acetic chloride in a reflux apparatus on the water-bath. It forms white crystals, melts at  $55^\circ$ , is sparingly soluble in alcohol, ether, and light petroleum, more readily soluble in chloroform. Its formation is of interest, as Nägeli found that camphoroxime is converted into its anhydride by the action of acetic chloride (this vol., 610).

*Diphenylacetoxime hydrochloride*,  $\text{CPh}_2\text{NOH}\cdot\text{HCl}$ , prepared by passing dry hydrochloric acid gas into a solution of diphenylacetoxime in anhydrous ether, forms a white crystalline powder; it is very unstable, losing hydrochloric acid on exposure to air.

*Diphenylsodacetoxime*,  $\text{CPh}_2\text{NONa}$ , is prepared by the action of sodium ethylate on an ethereal solution of diphenylacetoxime; it forms a white crystalline powder.

A. J. G.

**Methylene Blue and Allied Colouring Matters.** By A. BERNTHSEN (*Ber.*, 17, 611—620). In a former communication (this vol., 595), the author expressed the opinion that *thiodiphenylamine* would prove to be the parent substance to Lauth's violet and methylene blue; a supposition the truth of which is shown by the following results:—

When *thiodiphenylamine* is nitrated carefully by treatment with a nitric acid of sp. gr. 1.44, it yields two isomeric *dinitrodiphenylamine sulphoxides*, which are distinguished as  $\alpha$ - and  $\beta$ -compounds, the former is easily separated from the latter by its complete insolubility in boiling alcohol.

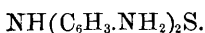
*Dinitrophenylamine sulphoxide*,  $\text{NH}(\text{C}_6\text{H}_3\text{NO}_2)_2\text{SO}$ , is soluble in hot aniline, from which it crystallises in yellowish-red needles or prisms. The  $\beta$ -compound separates from its alcoholic solutions as a light yellow powder.

$\alpha$ -*Dinitroacetyldiphenylamine sulphoxide*,  $\text{N}\overline{\text{Ac}} : \text{C}_{12}\text{H}_6(\text{NO}_2)_2 : \text{SO}$ , is formed when acetylthiodiphenylamine is nitrated; it is a light yellow powder consisting of slender, pale-yellow needles.

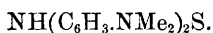
Methylthiodiphenylamine when nitrated yields compounds similar to the above.

Both the dinitro-compounds form leuco-bases when reduced with tin and hydrochloric acid or with stannous chloride; the  $\alpha$ -compound yielding the leuco-base of Lauth's violet, and the  $\beta$ -compound the leuco-base of a violet colouring matter isomeric with Lauth's violet. The colouring matter from the  $\beta$ -compound is a diacid base, whilst Lauth's violet is a monacid base, as shown by the composition of their hydrochlorides. That of the latter has the formula  $C_{12}H_9N_3S, HCl$ , and that of the former  $C_{12}H_9N_3S, 2HCl$ .

The view, already expressed by the author (*loc. cit.*), that methylene blue is a homologue of Lauth's violet, is supported by the fact that the leuco-bases of these colouring matters when treated with methyl iodide both yield one and the same compound, viz., *pentamethyl-di-amidothiodiphenylammonium iodide*, which would be formed from compounds having the constitution of these bases, as represented by the following formulæ:—



Lauth's white.



Methylene white.

P. P. B.

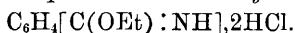
**Preparation of Phenylcyanamide.** By F. BERGER (*Monatsh. Chem.*, **5**, 217—219). Phenylcyanamide is most cheaply and conveniently prepared by dissolving monophenylthiocarbamide (50 grams) in excess of 30 per cent. potash by aid of heat, and adding a pretty concentrated hot aqueous solution of lead acetate (125 grams) in small portions and with constant shaking. When the liquid is quite cold, it is acidified with acetic acid to precipitate the phenylcyanamide. The yield is 75—80 per cent. of the theoretical. A. J. G.

**Derivatives of Isophthalonitrile and Terephthalonitrile.** By G. LUCKENBACH (*Ber.*, **17**, 1428—1437).—In order to study the behaviour of a dicyanide of the aromatic series with alcohol and hydrochloric acid, isophthalonitrile was prepared according to Barth and Senhofer's method (this *Jour.*, 1876, i, 585) by distilling potassium metabenzenedisulphonate with potassium cyanide. The product was, however, found to be contaminated with terephthalonitrile and could not be purified by crystallisation. The separation of the two bodies was finally accomplished by conversion into the thioamides and treatment with alcohol in which thioisophthalamide alone is soluble. From the separated thioamides, the nitriles were regenerated by boiling with a solution of lead acetate.

*Thioisophthalamide*,  $C_6H_4(CSNH_2)_2$ , prepared by the action of hydrogen sulphide on an alcoholic solution of the nitrile mixed with alcoholic ammonia, forms yellow crystals, melts with decomposition at 199—200°, the greater part decomposing into isophthalonitrile and carbon bisulphide, whilst a yellowish-brown resinous substance is left. It is sparingly soluble in ether and carbon bisulphide, more readily soluble in boiling alcohol.

*Isophthalimido ether*,  $C_6H_4[C(OEt):NH]_2$ .—A solution of isophthalonitrile in six parts of benzene is mixed with absolute alcohol and saturated with dry hydrochloric acid gas. After about half an hour the

liquid becomes turbid, an oil separates and after a short time solidifies to a crystalline mass of *isophthalimido ether hydrochloride*,



This, after purification, crystallises in white needles, softens at  $255^\circ$ , but is only completely fused at above  $270^\circ$ ; on further heating it is completely decomposed into ethyl chloride and isophthalamide. It is readily soluble in water, the solution soon decomposing into ammonium chloride and ethyl isophthalate. Better results are obtained in the preparation of the hydrochloride by using ethyl acetate in place of benzene as a solvent of isophthalonitrile. The *free base*, prepared by treating the hydrochloride with soda and ether, is readily soluble in alcohol and ether, melts at  $66^\circ$ , and on heating at  $120^\circ$  is decomposed into ethyl alcohol, isophthalonitrile, and gaseous products.

*Isophthalimido methyl ether* forms small needles melting at  $59$ — $62^\circ$ . The hydrochloride resembles the corresponding ethyl compound in preparation and properties.

*Isophthalamidine*,  $\text{C}_6\text{H}_4[\text{C}(\text{NH}_2) : \text{NH}]_2$ , is obtained as hydrochloride by the action of concentrated alcoholic ammonia on isophthalimido ethyl ether. The free base was only obtained in an impure state as a mass of small needles, insoluble in ether and benzene, soluble in water and alcohol, the solutions rapidly decomposing with evolution of ammonia. The hydrochloride,  $\text{C}_6\text{H}_4[\text{C}(\text{NH}_2) : \text{NH}]_2\text{HCl}$ , forms lustrous needles; the platinochloride,  $\text{C}_6\text{H}_4[\text{C}(\text{NH}_2) : \text{NH}]_2\text{H}_2\text{PtCl}_6$ , forms red crystals, sparingly soluble in water and alcohol; the sulphate crystallises in plates and is sparingly soluble in water; the nitrate is readily soluble in water and crystallises in needles. The silver derivative,  $\text{C}_6\text{H}_5\text{N}_4\text{Ag}_2$ , is obtained as an amorphous white precipitate, soluble in nitric acid and in ammonia.

By heating isophthalamidine with acetic anhydride and sodium acetate, it is converted into acetamide and a compound,  $\text{C}_{16}\text{H}_{15}\text{N}_5\text{O}_2 = \text{NH}[\text{C}(\text{NH})\cdot\text{C}_6\text{H}_4\cdot\text{CONH}_2]_2$ . This is insoluble in all ordinary solvents and is decomposed into isophthalic acid and ammonia when heated with potash or with hydrochloric acid.

*Isophthalimido thioethyl ether*,  $\text{C}_6\text{H}_4[\text{C}(\text{SEt}) : \text{NH}]_2$ .—The hydrochloride of this base is obtained by the action of hydrochloric acid gas on a solution of isophthalonitrile and mercaptan in ethyl acetate. It crystallises in nodules, and on heating turns yellow at  $175^\circ$ , and melts at  $190^\circ$ , with decomposition into ethyl chloride and thioisophthalamide. It is insoluble in ether, readily soluble in alcohol and water; an oil separates from the aqueous solution, which on being dried in a vacuum solidifies to a mass of small needles of *ethyl thioisophthalate*,  $\text{C}_6\text{H}_4(\text{COSEt})_2$ ; it is readily fusible. By the action of soda on the hydrochloride, isophthalimido ethyl ether is obtained as an oil soon solidifying to a crystalline mass. It is very unstable.

*Thioterephthalamide*,  $\text{C}_6\text{H}_4(\text{CS}\cdot\text{NH}_2)_2$ , is obtained as above described in the purification of isophthalonitrile. It forms a yellow powder insoluble in alcohol, and fuses with decomposition at  $263^\circ$ .

*Terephthalamidine*,  $\text{C}_6\text{H}_4[\text{C}(\text{NH}_2) : \text{NH}]_2$ .—By the action of hydrochloric acid and alcohol on the crude isophthalonitrile, a mixture of the imidoethers of iso- and terephthalic acids is formed, from which on

treatment with alcoholic ammonia *terephthalamidine hydrochloride* is obtained as a powder insoluble in absolute alcohol. It crystallises from water in brilliant hard apparently rhombic forms. The platinochloride forms small yellow crystals very sparingly soluble in water. The sulphate crystallises in small prisms and is sparingly soluble in water. The nitrate forms long thin needles. The free base could not be obtained in a pure state.

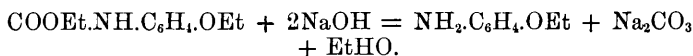
A. J. G.

**Action of Ethoxalyl Chloride on Diphenylthiocarbamide and Triphenylguanidine.** By M. v. STOJENTIN (*J. pr. Chem.* [2], 29, 302—303).—By the action of ethoxalyl chloride on diphenylthiocarbamide dissolved in benzene, a crystalline product is obtained of the composition  $C_{21}H_{17}N_3S_2O$ . On treating this with silver nitrate, the sulphur is removed, and diphenylparabanic acid (diphenyloxalyl-carbamide),  $CON_2Ph_2(C_2O_2)$ , is obtained. By the action of fuming nitric acid on the thio-compound,  $C_{21}H_{17}N_3S_2O$ , a nitro-derivative,  $C_{21}H_{12}N_6S_2O_6$ , is formed; this, when heated with water or alkalis yields paranitraniline. A product,  $C_{20}H_{16}N_3ClO$ , was obtained from triphenylguanidine and ethoxalyl chloride, which, on digestion with alcoholic potash or by means of sodium amalgam, loses chlorine with formation of triphenylguanidine. A crystalline product was also obtained from phenylcarbamide.

P. F. F.

**Parethoxyphenylurethane and some of its Derivatives.** By H. KÖHLER (*J. pr. Chem.* [2], 29, 257—256).—A number of derivatives have been prepared by the author with a view of ascertaining the influence exerted by the carbamic acid radicle on substitutions of the benzene nucleus.

Parethoxyphenylurethane,  $COOEt.NH.C_6H_4.OEt$ , is prepared by adding ethylic chlorocarbonate to an alcoholic solution of paramidophenetoil, precipitating the urethane by water, and recrystallising it from alcohol. It forms pink needles which melt at  $94^\circ$ . Long continued boiling with soda decomposes the urethane thus:—



When heated for several hours with strong hydrochloric acid at  $130^\circ$ , in a sealed tube, it is decomposed with formation of paramidophenol hydrochloride, carbonic anhydride, and ethyl chloride. The urethane distils between  $250^\circ$  and  $270^\circ$ , with partial decomposition, *parethoxycarbanil*,  $CON.C_6H_4.OEt$ , being formed by the elimination of alcohol. Parethoxycarbanil crystallises from glacial acetic acid in white needles melting at  $219^\circ$ ; it is exceedingly stable, and unlike ordinary carbanil does not combine with alcohol.

*Nitroparethoxyphenylurethane* is prepared by acting with concentrated nitric acid (sp. gr. 1.4) on the urethane at  $32-35^\circ$ , precipitating the nitro-compound by water, and crystallising it from alcohol. It forms long golden needles melting at  $71^\circ$ . As shown below, the nitro-group occupies the meta-position to the phenolic hydroxyl, and no isomeric mononitro-compound was found, but a small quantity of dinitroethoxyphenylurethane is formed. The mononitro-compound

may be more conveniently prepared than as above by heating 10 grams of the urethane with 150 grams of dilute nitric acid (sp. gr. 1.125) until the reaction becomes violent, after which no further heating is required.

*Amidoparethoxyphenylurethane hydrochloride* is prepared by reducing the nitro-compound with tin and hydrochloric acid. It crystallises in stellate groups of needles which melt at 155—156°, and dissolve both in water and alcohol; it reduces both silver nitrate and platinum chloride, and gives a blood-red coloration with bleaching powder or ferric chloride. The free amido-compound was obtained from the hydrochloride by neutralising a hot saturated solution of the latter with sodium carbonate; it separates out in small white needles which melt at 88°.

In order to ascertain the position in the benzene nucleus occupied by the nitro- and amido-groups in the above compounds, the diamidophenol was prepared from the amidoparethoxyphenylurethane by heating the hydrochloride with strong hydrochloric acid in a sealed tube for two hours at 130°. The tube was then opened to permit of the carbonic anhydride and ethyl chloride formed to escape, and thus prevent a secondary action by the latter taking place. The tube was then closed, and the heating repeated for periods of two hours at a time, until on opening the tube no further internal pressure was perceptible. The contents were then evaporated down in a current of sulphuretted hydrogen, and the hydrochloride of the diamidophenol obtained in small reddish-brown elongated scales. The diamidophenol was found to differ in several important points from that of Hemilian (this Journal, 1876, i, 918), thus the latter crystallises in small light grey prisms, and is insoluble in strong hydrochloric acid and in alcohol, whilst the diamidophenol from the urethane is soluble in both. Both diamidophenols give a dark-red coloration with chloride of lime or ferric chloride, but whereas that from the orthoparadiamidophenol of Hemilian has a violet tint, the other is of a pure blood-red colour. Since the two diamidophenols are not identical, the one obtained from the urethane must be parametadiamidophenol, and the nitro-group must have entered the urethane in the meta-position to the phenolic hydroxyl, as was to be anticipated.

*Diazoimidoethoxyphenylurethane*,  $\text{COOEt.N} < \text{C}_6\text{H}_3(\text{OEt}) > \text{N:N}$ , is formed by passing nitrous anhydride through a cold saturated solution of amido-ethoxyphenylurethane hydrochloride in absolute alcohol; the diazo-compound separates out in fine white crystals, which are insoluble in water and melt below 100°. The same compound separates out in white flocks when the hydrochloride of the amido-urethane is treated with an aqueous solution of potassium nitrite. Unlike other diazo-compounds, it neither explodes on heating nor by percussion, nor is it altered on heating with alcohol; on the other hand, when heated with a solution of ammonia or caustic soda, it is dissolved with evolution of nitrogen.

*Dinitroparethoxyphenylurethane* is prepared by acting with fuming nitric acid on the urethane in the cold, and precipitating with water and recrystallising from alcohol. It forms minute interlaced needles

of a yellowish-white colour, melting at  $141^{\circ}$ . A second dinitro-compound was obtained from the alcoholic mother-liquors of the above, it forms bright yellow needles of considerable length, melting at  $121^{\circ}$ . The third possible dinitro-urethane was not found.

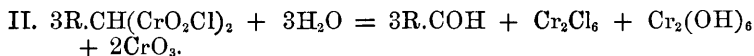
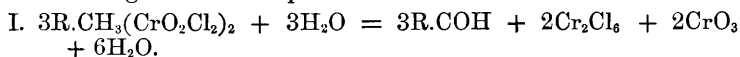
*Diamidoparethoxyphenylurethane hydrochloride* was prepared from the first of the above dinitro-urethanes by the action of tin and hydrochloric acid. The diamido-urethane combines with only 1 mol. HCl, and this salt crystallises in dark-coloured hexagonal scales melting at  $238^{\circ}$ .

*Trinitroparethoxyphenylurethane* was prepared in the same manner as the dinitro-compounds, only that the reaction was assisted by heat. It crystallises in small bright yellow prismatic needles, melting with decomposition at  $211$ – $212^{\circ}$ . The trinitro-compound may be more conveniently prepared by heating 10 grams of the urethane with 200 grams of nitric acid (sp. gr. 1.4). All attempts to further nitrate the trinitro-urethane proved abortive. By reduction with tin and hydrochloric acid, the trinitro-compound was converted into *triamidoparethoxyphenylurethane hydrochloride*, which crystallises in small brownish needles, melting with decomposition at  $233^{\circ}$ .

*Trinitroamidophenetöl*,  $C_6H(NH_2)(NO_2)_3.OEt$ , was prepared by heating the trinitro-urethane with 20 times its weight of sulphuric acid (sp. gr. 1.14) for 3–5 hours in a large flask with an inverted condenser; the product was, however, not obtained in a pure state, but mixed with some of the unchanged trinitro-urethane. The crude product was converted by means of tin and hydrochloric acid into *tetramidophenetöl hydrochloride*,  $C_6H(NH_2)_4.OEt, 2HCl$ ; this crystallises in long flat prisms, which do not melt at  $360^{\circ}$ . With chloride of lime or ferric chloride, it gives a dark green coloration, changing to red, reddish-brown, yellow, and finally becomes colourless again.

P. F. F.

**Étard's Reaction for the Preparation of Aromatic Aldehydes.** By E. BORNEMANN (*Ber.*, 17, 1462–1475).—Étard has shown (*Abstr.*, 1881, 581) that chromyl dichloride unites with aromatic hydrocarbons to form compounds which, when decomposed with water, yield aldehydes if the hydrocarbon contains a methyl-group, and ketones if no methyl-group is present. These compounds are of two kinds, the one class being simply additive products of the hydrocarbon and chromyl chloride, the other containing two hydrogen- and two chlorine-atoms less. The decomposition into aldehyde takes place according to the two equations:—



Étard states, that with a mixture of the isomeric xylenes, chromyl dichloride forms a product which is decomposed by water, yielding pure metatoluyaldehyde. The author has repeated this reaction, but has always obtained a mixture of the isomeric aldehydes.

*Metatoluyaldehyde*,  $C_6H_4Me.CO.H$ .—35 parts of pure xylene and 100

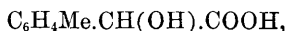


of chromyl dichloride were each diluted with carbon bisulphide, and then gradually mixed, the red colour of the mixture disappears slowly, and a brown crystalline precipitate of the formula  $C_6H_4Me_2 \cdot 2CrO_2Cl_2$  is deposited. The temperature of the solution must not be allowed to exceed  $47^\circ$ , or dangerous explosions may occur. The brown precipitate is filtered off and dried rapidly by agitation over the water-bath in a flask connected with an air-pump. The heating over the water-bath must not be continued long, or violent explosions may take place. The cause of these explosions could not be ascertained, as small portions of this compound may be heated to  $180$ — $200^\circ$  without change, and only give off hydrochloric acid when heated over  $200^\circ$ . The dried substance is then added to water in small quantities, and the aldehyde separated by distillation with steam or extraction with ether. It is then purified by means of its compound with hydrogen sodium sulphite. Metatoluylaldehyde is a colourless, highly refracting oil which boils at  $198$ — $199^\circ$ , has the odour of bitter almonds and the properties ascribed to it by Gundelach (*Bull. Soc. Chim.*, 1867, **26**, 44) and Étard (*loc. cit.*). It rapidly absorbs oxygen from the air, and is converted into metatoluic acid melting at  $109$ — $110^\circ$ .

*Orthotoluylaldehyde* was prepared from orthoxylene in a similar manner. It boils at  $199$ — $200^\circ$ , has the odour of bitter almonds, and yields orthotoluic acid melting at  $103^\circ$ .

*Paratoluylaldehyde* has an odour like pepper, boils at  $204$ — $205^\circ$ , and yields paratoluic acid melting at  $180^\circ$ . The yield of aldehydes in these three cases was about 70—80 per cent. of the theoretical.

*Metaxyliidenephnylhydrazine*,  $C_6H_4Me.CH : N_2Ph$ , is formed by the action of metatoluylaldehyde on phenylhydrazine, using equal molecular weights. It crystallises in yellow prisms which melt at  $91^\circ$ . It is sparingly soluble in water, but easily so in the other usual solvents. *Metaxyliidenaniline*,  $C_6H_4Me.CH : NPh$ , is obtained by mixing together the aldehyde and aniline. It is a mobile oil of aromatic odour, and boils at  $313$ — $314^\circ$ . It is split up again into its two components by mineral acids and oxalic acid, but is not acted on by acetic or tartaric acid. *Metamethylmandelonitrile*,  $C_6H_4Me.CH(OH).CN$ , is obtained as a colourless mobile oil when the necessary quantity of hydrochloric acid is added to a mixture of equivalent proportions of metatoluylaldehyde and powdered potassium cyanide. Hydrochloric acid dissolves it at  $60$ — $70^\circ$  with partial decomposition, and the solution yields small quantities of the corresponding amide when neutralised with ammonia. Strong sulphuric acid dissolves it with a red coloration, and water then precipitates a yellow voluminous mass having acid properties. *Metamethylmandelic acid*,



is obtained from the above nitrile by heating it with fuming hydrochloric acid at  $60$ — $70^\circ$ . It crystallises in small glistening white scales which are easily soluble in water, alcohol, ether, chloroform, and boiling benzene, and melt at  $84^\circ$ . Cupric sulphate added to an aqueous solution of the ammonium salt, gives a blue precipitate soluble in ammonia; lead, silver, and zinc salts give white precipitates; the barium salt crystallises from water in small nodules. *Metatoluyl-*

*anilidoacetonitrile*,  $C_6H_4Me.CH(NHPh).CN$ , was obtained by heating an ethereal solution of the nitrile described above with aniline in closed tubes at  $100^\circ$ . It crystallises from alcohol in small colourless glittering scales, which melt at  $95^\circ$ , and are sparingly soluble in light petroleum, insoluble in water. Its alcoholic solution decomposes slowly with evolution of hydrocyanic acid. *Metatoluylanilidoacetamide*,  $C_6H_4Me.CH(NHPh).CONH_2$ , is obtained by dissolving the corresponding nitrile in sulphuric acid, allowing the solution to remain for 24 hours, then pouring it into water, and saturating with ammonia. It crystallises in white lustrous scales or needles which melt at  $127$ — $128^\circ$ , and are easily soluble in alcohol, ether, benzene, and chloroform, insoluble in water. *Metatoluylanilidoacetic acid*,



was prepared by digesting the amide with dilute sulphuric acid. It crystallises in small silvery scales which are easily soluble in the usual solvents, and melt at  $137$ — $139^\circ$ . Its salts with mineral acids are unstable, those with metals stable. *Metatoluylamidoacetic acid*,  $C_6H_4Me.CH(NH_2).COOH$ .—Metamethylmandelonitrile is digested with alcoholic ammonia in closed tubes at  $100^\circ$ , and the resulting dark-red liquid, which contains the amidated nitrile, is decomposed with dilute sulphuric acid. This acid crystallises in microscopic white hexagonal scales which are almost insoluble in the ordinary solvents. If heated with care, it sublimes at about  $230^\circ$ , but decomposes if heated quickly. Its copper, zinc, lead, and silver salts are white, and sparingly soluble in water. By the nitration of metatoluylaldehyde the author has obtained *orthonitrometatoluylaldehyde*—a pale-yellow oil already described (*Ber.*, **16**, 817), and *dinitrometatoluylaldehyde*, crystallising in long silky white needles which melt at  $110$ — $112^\circ$ , and are easily soluble in alcohol, ether, benzene, and chloroform, sparingly so in boiling water. When treated with acetone and dilute alkali, it yields a colouring matter belonging to the indigo-group, so that one nitro-group must be in the para-position to the aldehyde-group. *Metamethylcinnamic acid*,  $C_6H_4Me.CH:CH.COOH$ , was prepared by heating together 4 parts metatoluylaldehyde, 3 parts dry sodium acetate, and 10 parts acetic anhydride. It crystallises in well-formed thin silky needles melting at  $110$ — $111^\circ$ . It is easily soluble in alcohol, ether, chloroform, benzene, and boiling water, sparingly so in light petroleum. A solution of its ammonium salt yields a characteristic yellow precipitate with ferric chloride: its copper salt is pale blue, its lead salt is white. With a cold solution of silver nitrate, it gives a white curdy precipitate which may be recrystallised from boiling water, but the recrystallised salt is not nearly as stable as that precipitated in the cold.

L. T. T.

**Action of Benzoic Chloride on Benzaldehyde in Presence of Zinc-dust.** By C. PAAL (*Ber.*, **17**, 909—911).—The action of acetic chloride on benzaldehyde in presence of zinc-dust has been previously studied (*Abstr.*, 1883, 805). In the case of benzoic chloride the product of the reaction is found to consist of two bodies, one sparingly soluble even in hot acetic acid, the other easily soluble. The insoluble

body melts at  $246^{\circ}$ , crystallises in white needles, and has the composition  $C_{28}H_{22}O_4$ . With alcoholic potash solution, it yields hydrobenzoïn and benzoic acid, and is therefore the hydrobenzoïn bibenzoate first prepared by Forst and Zincke.

The soluble body melts at  $151^{\circ}$ , and has the same composition as the above. On treating it with alcoholic potash and then with water, crystals of isohydrobenzoïn separate, and the solution contains sodium benzoate; the body is therefore isohydrobenzoïn bibenzoate, also prepared by Forst and Zincke.

H. B.

**Condensation-product from Salicylaldehyde.** By H. SCHIFF (*Ber.*, **17**, 770—771).—Bourguin has recently (next Abstract) described a product obtained by the action of zinc chloride on salicylaldehyde. A similar compound was described by the author in 1872, and the formula  $C_{14}H_{10}O_3$  assigned to it. It was obtained by the action of phosphorous oxychloride on helicin, and more slowly by using salicylaldehyde; it cannot again be converted into salicylaldehyde. Bourguin's analyses also confirm the formula  $C_{14}H_{10}O_3$ , which may perhaps be written  $HO.C_6H_4.CO.C_6H_4.CO.H$ ; but as the body does not give any aldehyde reactions it probably consists of two such molecules united together by the aldehyde-groups. It possibly belongs to the class of condensation-products obtained by Baeyer (1872) from phenols and aldehydes.

H. B.

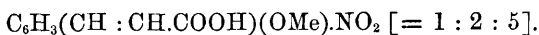
**Action of Zinc Chloride on Salicylaldehyde and Parahydroxybenzaldehyde.** By A. BOURQUIN (*Ber.*, **17**, 502—504).—Both these aldehydes, when heated with glacial acetic acid and zinc chloride, form red amorphous substances,  $C_{14}H_{10}O_3$ , insoluble in ordinary solvents and slightly soluble in chloroform. They are both soluble in caustic alkalis, the product from salicylaldehyde forming red solutions, whilst that from parahydroxybenzaldehyde gives a violet solution. Further, the former is distinguished from the latter product by its solubility in sodium hydrogen sulphite solution, and by forming an acetyl derivative when heated with acetic anhydride. These compounds, formed by the condensation of 2 mols. of the aldehydes, are isomeric with benzoylsalicylaldehyde ( $BzO.C_6H_4.CO.H$ ) and Perkin's disalicyl hydride,  $(COH.C_6H_4)_2O$ ; their constitution is most probably represented by the following formula:  $(OH.C_6H_4.C)_2O$ , which represents them as a species of glycid compound in the formation of which the aldehyde-groups alone take part.

P. P. B.

**Nitromethylsalicylaldehyde and its Derivatives.** By A. SCHNELL (*Ber.*, **17**, 1381—1358).—These experiments were undertaken (in connection with those of Tiemann and Ludwig—*Abstr.*, 1883, 188—on metahydroxybenzaldehyde) to ascertain if the nitro-group could be replaced by hydroxyl or methoxyl. Metanitromethylsalicylaldehyde was prepared by Voaswinkel (*Abstr.*, 1883, 189); it has the constitution  $C_6H_3(COH)(OMe).NO_2$  [= 1 : 2 : 5]. All attempts to convert it into a hydroxylated methylsalicylaldehyde by amidation, conversion into the diazo-compound, &c., were fruitless.

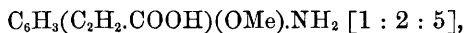
By treatment with ferrous sulphate and ammonia, a crystalline substance, showing the properties both of an amine and an aldehyde, was formed, but was too unstable and obtained in too small quantity to serve as the material for the preparation of a hydroxymethylsalicylaldehyde. This method showing no prospect of success, the substances required were prepared by conversion of the aldehyde into cinnamic acid, and, after substitution, reconversion of this into the substituted aldehyde.

*Metanitro-orthomethoxycinnamic acid,*



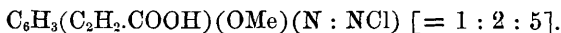
Metanitromethylsalicylaldehyde is converted into the corresponding cinnamic acid by heating it with acetic anhydride and sodium acetate. The acid crystallises in small white needles, melts at  $238^\circ$ , is readily soluble in ether and alcohol, and sparingly soluble in cold water. A neutral solution of the ammonium salt gives the following precipitates with metallic solutions:—With barium chloride white, soluble in hot water; with calcium chloride white, readily soluble; with lead acetate white, voluminous, dissolves on heating, then resinifies; with copper sulphate, greenish-blue, nearly insoluble; and with silver nitrate a white, very sparingly soluble salt.

*Metamido-orthomethoxycinnamic acid,*

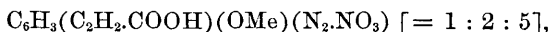


prepared by reduction of the nitro-acid with ammonia and ferrous sulphate, crystallises in pale-red needles, melts at  $189^\circ$ , is nearly insoluble in cold water, somewhat more readily in hot water, readily soluble in alcohol and ether. The ammonium salt gives a voluminous white precipitate with silver salts which resinifies on heating; a yellow precipitate with lead salts; a dark-green precipitate with copper sulphate, nearly insoluble in hot water; a white precipitate with zinc salts.

*Orthomethoxycinnamic acid metadiazochloride,*



1 part of the amido-acid is rubbed to a paste with 3 parts of concentrated aqueous hydrochloric acid and a solution of half part of sodium nitrite in 10 parts of water added in portions with constant stirring; the dark red-brown solution obtained deposited yellow crystals of the diazo-chloride on long standing. It is decomposed by heating at  $102^\circ$ . The corresponding *nitrate*,



prepared by the action of nitric acid on the chloride, crystallises in yellow needles, explodes on heating to  $151$ – $152^\circ$ , is nearly insoluble in cold water, alcohol, and ether, somewhat soluble in hot water.

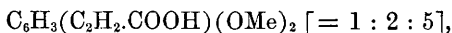
*Metalhydroxyorthomethoxycinnamic acid,*



prepared by boiling the diazo-nitrate or chloride with water, forms

small yellow crystals, melts at 179–180°, is nearly insoluble in cold water, readily soluble in alcohol, ether, benzene, and hot water. Solutions of the ammonium salt give a yellow precipitate with barium salts; a yellow precipitate with silver nitrate; a reddish-white precipitate with lead acetate; a clear green precipitate with copper sulphate; insoluble in hot water; soluble in ammonia, with yellowish-red colour. Fusion with potash converts the acid into a mixture of dihydroxybenzoic acid and other products.

*Metaorthodimethoxycinnamic acid*,



is obtained by the action of methyl iodide and methyl alcohol on the dipotassium salt of the preceding acid, the product being treated with potash to decompose the methyl salt first formed. It crystallises in clear yellow needles, and melts at 143°. The ethereal solution shows a green fluorescence. A solution of the ammonium salt gives a white precipitate with lead acetate; with cupric sulphate a bluish-green precipitate insoluble on boiling; and a white precipitate with silver nitrate.

By oxidation with potassium permanganate, the dimethyl acid is readily converted into dimethylgentisic aldehyde,



the constitution of which has been worked out by Tiemann and Max-Müller (Abstr., 1882, 52).

A. J. G.

**Condensation of Acetone with Aromatic Aldehydes.** By L. CLAISEN and A. C. PONDER (*Annalen*, **223**, 137–148).—The *Benzalacetone*,  $\text{COMe}.\text{CH}:\text{CHPh}$ , which Claisen and Claperède (Abstr., 1882, 511) obtained by the action of zinc chloride on a mixture of benzaldehyde, acetone, and acetic anhydride, is identical with the acetocinnamone described by Engler and Leist (this Journal, 1873, 901). It is best prepared by adding 20 parts of a 10 per cent. solution of sodium hydroxide to 1800 parts of water containing 20 parts of benzaldehyde and 40 of acetone. After an interval of three or four days the mixture is extracted with ether. The ethereal solution is dried over calcium chloride and distilled in a vacuum, when a small quantity of dibenzalacetone is left in the retort. Benzalacetone boils at 152° under a pressure of 25 mm., and at 261° under the ordinary atmospheric pressure. Many of the properties of this compound have been previously described (*loc. cit.*).

*Dibenzalacetone* or *cinnamone*,  $\text{CO}(\text{CH}:\text{CHPh})_2$  (Abstr., 1882, 511), can also be prepared by acting on an alcoholic solution of benzaldehyde and acetone with caustic soda. The crystalline mass, which is slowly deposited, is washed with alcohol and recrystallised. A better yield is obtained by mixing together 7 parts of monobenzalacetone, 5 of benzaldehyde, 200 of water, 150 of alcohol, and 20 parts of a 10 per cent. solution of soda. Dibenzalacetone crystallises in monoclinic plates,  $a : b : c = 4.886 : 1 : 1.378$ .  $\beta = 78^\circ 43'$ . The crystals melt at 112° with decomposition.

Traces of acetone may be detected in alcoholic solution by the addi-

tion of a few drops of benzaldehyde and sodium hydroxide. After a few hours the characteristic crystalline plates of dibenzalacetone are deposited.

The preparation and properties of *monofurfuralacetone* have been previously described by the authors (Abstr., 1882, 513). *Difurfuralacetone*,  $\text{CO}(\text{CH}:\text{CH}.\text{C}_4\text{H}_3\text{O})_2$ , is prepared by adding 30 grams of a 10 per cent. solution of caustic soda to a mixture of 20 grams of furfuraldehyde, and 6 of acetone, dissolved in 400 c.c. of water and 500 of alcohol. After an interval of several days, the liquid is poured into water. The crude product is recrystallised from light petroleum, and is then obtained in brown prisms, which melt at  $60^\circ$  and dissolve freely in alcohol, ether, and chloroform.

*Benzalfurfuralacetone*,  $\text{CHPh}:\text{CH}.\text{CO}.\text{CH}:\text{CH}.\text{C}_4\text{H}_3\text{O}$ , formed by the action of dilute caustic soda on an alcoholic solution of furfuralacetone and benzaldehyde, or of benzalacetone and furfuraldehyde, crystallises in straw-coloured plates or flat prisms melting at  $56^\circ$ . The crystals are soluble in alcohol, ether, benzene, chloroform, and give a dark red coloration with sulphuric acid.

Cuminol forms two compounds with acetone, viz., *cuminalacetone*,  $\text{C}_3\text{H}_4(\text{C}_{10}\text{H}_{12})\text{O}$ , a strongly refractive oily liquid boiling at  $180^\circ$  under a pressure of 23 mm., and *dicuminalacetone*,  $\text{C}_3\text{H}_2(\text{C}_{10}\text{H}_{12})_2\text{O}$ , crystallising in long prisms melting at  $106^\circ$ .

Benzalacetophenone can also be prepared by adding soda to acetophenone and benzaldehyde dissolved in a mixture of alcohol and water.

W. C. W.

**Action of Acetic Chloride on Benzophenone in Presence of Zinc-dust.** By C. PAAL (*Ber.*, 17, 911—913).—The reaction in ethereal solution is energetic, a white crystalline compound of the composition  $\text{C}_{26}\text{H}_{20}\text{O}$  being deposited, it melts at  $178$ — $179^\circ$ ; with alcoholic potash, it yields triphenylmethane and benzoic acid; it is  $\beta$ -benzopinacoline (Abstr., 1881, 813). The yield is excellent if an excess of acetic chloride—viz., about four times the theoretical quantity—be employed. If the theoretical quantity of acetic chloride is used, the product consists mainly of  $\alpha$ -benzopinacoline, forming long needles and melting at  $196^\circ$ . By employing about twice or two and a-half times the theoretical amount of acetic chloride, a body is obtained melting constantly at  $158$ — $159^\circ$ ; it is, however, a mixture of the  $\alpha$ - and  $\beta$ -benzopinacoline.

In this reaction benzopinacone biacetate seems to be formed, but at once decomposes into acetic anhydride and  $\alpha$ -benzopinacoline, which is converted into  $\beta$ -benzopinacoline by the excess of acetic acid.

H. P.

**Benzoylacetone and Isonitrosobenzoylacetone.** By M. CERESOLE (*Ber.*, 17, 812—817).—By the action of hydroxylamine hydrochloride on benzoylacetone,  $\text{COPh}.\text{CH}_2.\text{COMe}$ , a crystalline substance melting at  $65.5$ — $66^\circ$  is formed; it does not contain the isonitroso-group twice, but only once, and unlike all such compounds (this vol., 599) it is quite insoluble in acids and in alkalis. The action of alkalis should decide which of the two possible isomerides the body is, viz.,  $\text{COPh}.\text{CH}_2.\text{CMe}:\text{NOH}$ , or  $\text{CPh}(\text{NOH}).\text{CH}_2.\text{COMe}$ , the

reaction, however, was not very sharp, but pointed rather to the second formula. Attempts to act on the second carbonyl-group were quite unsuccessful; this is remarkable, the more so since by the action of phenylhydrazine on orthonitrobenzoylacetone both carbonyl-groups are attacked.

In order to ascertain if hydroxylamine would act on both carbonyl-groups in certain derivatives of benzoylacetone, use was made of isonitrosobenzoylacetone,  $\text{CPh.C(NO.H).COMe}$ , since this also promised to give the first of a new class of bodies, the trioximides.

*Isonitrosobenzoylacetone* is not formed by the action of alkalis and nitrous acid on ethylic benzoylacetate; but it is easily prepared by adding sodium alcoholate, and then nitrous acid, to an alcoholic solution of benzoylacetone. It crystallises from hot water in needles melting at  $123.5-124^\circ$ . It yields hydroxylamine hydrochloride when heated with strong hydrochloric acid. Heated with hydroxylamine and hydroxylamine hydrochloride a body is obtained, which, after purification, melts at  $178^\circ$ , and contains the isonitroso-group, not thrice, but only twice. Another substance melting about  $115^\circ$ , formed at the same time, was also found not to be the desired



since it contains the isonitroso-group twice; it is probably one or other of the two possible isomerides,  $\text{CPh(NO.H).C(NO.H).COMe}$ , and  $\text{COPh.C(NO.H).COMe:NOH}$ .  
H. B.

**Phenyl Thienyl Ketone.** By A. COMEY (*Ber.*, 17, 790—791).—The author has been unable to complete his investigation to ascertain whether thiophene undergoes the Friedel-Crafts reaction, but communicates the following. Crude thiophene (*Abstr.*, 1883, 1091) heated with benzoic chloride and aluminium chloride yields phenyl thienyl ketone,  $\text{C}_6\text{H}_5\text{CO.C}_4\text{H}_3\text{S}$ , which is separated by distillation with steam and extraction of the distillate with ether; it melts at  $55^\circ$ , and boils at about  $300^\circ$ . When heated in alcoholic solution with hydroxylamide hydrochloride and caustic soda, *phenylthienylacetoxime*,



is obtained in colourless crystals melting at  $91-92^\circ$ . The ketone, when heated with soda-lime, yields calcium benzoate, free from sulphur; the oily distillate is not pure thiophene, but contains benzene. Phenyl thienyl ketone gives a blue coloration with isatin and sulphuric acid; the acetoxime, a violet coloration.  
H. B.

**Substances accompanying Benzoic Acid prepared from Gum Benzoin.** By O. JACOBSEN (*Arch. Pharm.* [3], 22, 366—374).—On treating benzoic acid from gum benzoin with sodium carbonate solution, an oil is left undissolved, smelling of vanillin and also of phenol. By fractionation, it may be separated into three principal portions, boiling at  $200-210^\circ$ ,  $235-245^\circ$ , and  $280-330^\circ$ , and a pitch-like residue not further examined. The first fraction consists of methyl benzoate and guaiaicol, which can be separated by treatment with cold dilute caustic soda. The second and smaller fraction, when

shaken with water, gives up catechol in the aqueous solution; the portion insoluble in water and dilute alkalis is acetylguaiacol (Abstr., 1882, 54). The third and largest portion consists of an oil, insoluble in dilute alkalis, which by saponification with alcoholic potash, and subsequent treatment with water and ether, yields benzyl alcohol, and benzophenone, whilst the aqueous solution contains guaiacol and benzoic acid; this fraction therefore contains benzyl benzoate, benzophenone, and benzoylguaiacol. The oil also contains vanillin, but in minute quantity only. The medicinal value of sublimed benzoic acid is attributed to the catechol and guaiacol; it is believed that of the above bodies only vanillin and benzyl benzoate exist ready formed in the gum. Benzaldehyde may be formed by the oxidation of the contained benzyl benzoate, so that the production of the former cannot be considered as a proof of adulteration with cinnamic acid. Schickum and Schneider (Abstr., 1882, 1138) have tested the genuine nature of natural benzoic acid by its reducing boiling ammoniacal silver solution; but catechol will reduce the solution in the cold, and the author therefore suggests the following method of testing:—Convert the benzoic acid into the sodium salt, and, after drying, shake with ether; after removal of the ether, the residue may be dissolved in water, and the above or any other tests for catechol applied.

H. B.

**Aromatic Acids as Dye-forming Substances.** By C. ZULKOWSKY (*Monatsh. Chem.*, 5, 221—227).—A mixture of benzoic acid (1 mol.) and resorcinol (2 mols.) is heated for 6 to 8 hours at 170—180° with an amount of zinc chloride equal in weight to the resorcinol employed. After washing several times with water, the residue is dissolved by boiling it with 50 per cent. alcohol. On cooling, crystals separate; these are much less soluble in alcohol than the crude product, and their solution has a golden-yellow colour, with a bright green fluorescence, which becomes much stronger on addition of ammonia or potash. Sulphuric acid can be used instead of zinc chloride as the dehydrating agent. From its method of preparation this substance should be identical with Doebner's resorcinolbenzein (Abstr., 1880, 644). Benzoic anhydride can be substituted for the acid when zinc chloride is employed.

By heating benzoic acid (1 mol.), orcinol (2 mols.), and sulphuric acid for about four hours at 130—135°, there is obtained, after washing with hot water, a steel-green brittle mass, of metallic lustre. This, after purification by boiling with an amount of dilute soda, insufficient for complete solution, and precipitation with acetic acid, forms a golden-yellow precipitate, whose alcoholic solution has a golden-yellow colour and a feeble dark green fluorescence, increased by ammonia. The substance can be crystallised from glacial acetic acid.

The product obtained by heating benzoic acid (1 mol.) with pyrogallol (2 mols.) and sulphuric acid for 2½ hours at 120—130° is soluble in hot water, from which it separates in large crystals on cooling. The crystals appear to be really colourless, but are covered by a brown layer, apparently formed by an oxidation-product. The



alcoholic solution has a brownish-red colour; it turns violet with ammonia, whilst potash produces discoloration.

Salicylic acid and resorcinol heated with zinc chloride or sulphuric acid at 130—140° give a substance forming dark reddish-brown crystals. The alcoholic solution has a red-yellow colour, and shows a green fluorescence which becomes extraordinarily intense on adding ammonia.

A. J. G.

**Action of Reducing Agents on Ortho-nitrophenoxyacetic Acid.** By A. THATE (*J. pr. Chem.* [2], 29, 145—191).—This subject was first investigated by Fritzsche (Abstr., 1880, 318), who employed stannous chloride as the reducing agent, and obtained a product which he named orthamidophenoxyacetic acid. The author finds that the product obtained according to Fritzsche's instructions is never a pure orthamidophenoxyacetic anhydride, but always contains more or less chlorine not separable by recrystallisation.

*Orthonitrophenoxyacetic acid*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH}$ .—Fritzsche's method of evaporating a solution of sodium monochloracetate with sodium orthonitrophenylate gives but a very small yield, owing to most of the nitrophenol becoming liberated and volatilised. A much better process is to heat equivalent weights of sodium orthonitrophenylate in saturated solution with sodium monochloracetate for 10 hours at 100° in a flask provided with a reflux condenser. The reaction is complete when the wine-red colour of the liquid is changed to yellow or yellowish-red. The filtered liquid is acidulated with hydrochloric acid, and the precipitated acid is purified by recrystallisation from water. The acid is yellowish-white, melts at 156·5°, and crystallises in irregular pyramids, which exhibit double refraction, and therefore do not belong to the regular system, as stated by Fritzsche.

*Azoxyorthophenoxyacetic acid*,  $(\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH})_2\text{N}_2\text{O}$ .—Prepared by the action of sodium amalgam on a solution of sodium orthonitrophenoxyacetate. The solution is poured off from the separated mercury, and solidifies to a yellow mass on cooling, which is collected, is decomposed by acid, and recrystallised from dilute alcohol. The substance so obtained is a mixture of azoxy- and azo-orthophenoxyacetic acid. If the reduction has taken place satisfactorily, the melting point of the substance should not be below 170°. In order to purify the azoxy-acid, it is etherified by means of alcohol and hydrochloric acid gas; the ether crystallises out on cooling, and is separated from the corresponding ether of the azo-acid by washing with dilute acid. The ether is then saponified, the potassium salt decomposed with hydrochloric acid and the azoxyorthophenoxyacetic acid recrystallised from water. The acid crystallises with 1 mol.  $\text{H}_2\text{O}$  in forms which resemble those of calc spar; it is insoluble in anhydrous ether and benzene, and melts at 186—187°. The acid forms a normal and an acid silver salt, both of which are anhydrous, whilst the barium salt contains 2 mols.  $\text{H}_2\text{O}$ . The ethylic ether crystallises in long white silky needles melting at 113—114°.

*Azo-orthophenoxyacetic acid*,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{CH}_2\cdot\text{COOH})_2\text{N}_2$ .—The preparation is similar to that of the azoxy-acid, excepting that more sodium-

amalgam has to be employed. The acid can generally be obtained in a pure state by three or four recrystallisations from dilute alcohol, but it cannot be separated from the azoxy-acid by means of its ethylate, as the latter is very difficult to obtain in a pure state; the two acids may, however, be approximately separated by means of their silver salts, that of the azo-acid being precipitated from a hot aqueous solution, whilst the silver salt of the azoxy-acid only falls out on cooling. The azo-acid crystallises with 2 mols.  $\text{H}_2\text{O}$  in beautiful silky orange needles melting at  $162^\circ$ . It is soluble in water, alcohol, ether, alkalis, and strong acids. The salts are of a bright yellow or red colour; the potassium, sodium, and silver salts each crystallise with 3 mols.  $\text{H}_2\text{O}$ , the barium salt with  $2\text{H}_2\text{O}$ , and the calcium salt with  $8\text{H}_2\text{O}$ . The diethylate melts at  $110$ – $111^\circ$ .

*Hydrazo-orthophenoxyacetic acid*,  $(\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH})_2$ , is prepared by saturating a solution of azo-orthophenoxyacetic acid with sulphuretted hydrogen, and allowing the mixture to remain for some time in a closed flask; the ammonium salt of the hydrazo-acid then separates out mixed with sulphur, and is purified by recrystallisation from alcohol. The ammonium salt is only partially converted into the free acid by acidulation with acetic acid, an acid salt being the chief product. The potassium salt crystallises with 3 mols.  $\text{H}_2\text{O}$ ; on drying in contact with air, it partially passes into the potassium salt of the azo-acid, acquiring thereby a vermilion colour. Mineral acids, on the other hand, precipitate the azoxy-acid from the aqueous solutions of salts of the hydrazo-acid.

*Orthamidophenoxyacetic acid*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH}$ .—The acid itself is as yet unknown, for it decomposes into 1 mol.  $\text{H}_2\text{O}$  and a body which, from its mode of formation, may be termed orthamidophenoxyacetic anhydride,  $\text{C}_6\text{H}_7\text{NO}_2$ . This substance is obtained as a bye-product in the preparation of azo-orthophenoxyacetic acid. The filtrate from the sodium salt of this acid, which separates after the reduction is complete as described above, is acidulated with hydrochloric acid and evaporated to dryness, the residue then consists of sodium chloride together with the azo-acid and the amido-anhydride. The amido-anhydride is extracted by absolute alcohol, and is separated from the azo-acid by crystallisation from water, and afterwards from dilute alcohol. The anhydride crystallises in short white prisms melting at  $166$ – $167^\circ$ . It is also formed when orthonitrophenoxyacetic acid is reduced with iron filings and acetic acid. It was not found possible to convert the anhydride into monochlororthamidophenoxyacetic acid by continued boiling with hydrochloric acid; this compound,  $\text{C}_6\text{H}_6\text{ClNO}_2$ , is however formed, and crystallises out when an aqueous solution of orthonitrophenoxyacetic acid is reduced with stannous chloride; it is purified by repeated crystallisation from water, and has a melting point of  $196$ – $197^\circ$ . Several salts of the two acids from which these anhydrides are respectively derived are then described.

The author points out that the substance previously obtained by Fritzsche, and melting at  $143$ – $144^\circ$ , may possibly consist of 1 mol. of orthamidophenoxyacetic anhydride, and 1 mol. of monochlororthamidophenoxyacetic anhydride ( $\text{C}_6\text{H}_7\text{NO}_2 + \text{C}_6\text{H}_6\text{ClNO}_2$ ), and that if

this be the case it is not improbable that pairs of molecules of one and the same anhydride may be similarly linked together, thus:  $(C_8H_7NO_2)_2$  and  $(C_8H_6ClNO_2)_2$ . Owing to the instability of these compounds it was not found possible to test this hypothesis by means of vapour-density determinations. Assuming, however, this proposition to be true, the so-called "inner anhydrides" can be readily derived from the hydrazo-compounds, a step which is apparently justified on the one hand by the intermediate position which they occupy between the hydrazo- and the amido-compounds, and on the other by the instability which the hydrazo-compounds exhibit.

P. F. F.

**Constitution of Dibromanisic Acid.** By L. BALBIANO (*Gazzetta*, 14, 9—12).—From the results obtained by the destructive distillation of calcium dibromanisate and of a mixture of sodium dibromanisate with lime (Abstr., 1883, 1125), the author inferred that the bromine-atom occupied the ortho-position relatively to the methyl-group or to the carboxyl-group. A study of the action of nitric acid on dibromanisic acid has now enabled him to definitely determine the constitution of the latter.

On adding dibromanisic acid (5 grams) to nitric acid of sp. gr. 1.52 (35 to 40 grams), at a temperature of  $30^\circ$  to  $40^\circ$ , it dissolves with effervescence, due to evolution of carbonic anhydride, and the solution becomes red; on pouring this into a large quantity of water, a white crystalline substance is precipitated about equal in weight to the dibromanisic acid originally employed. The product when purified by crystallisation from a mixture of ether and alcohol melts at  $122$ — $123^\circ$ , and has all the properties of the anisole derivative obtained by Koerner (*Gazzetta*, 4, 390) from Brunck's dibromonitrophenol, and which has the constitution  $[OMe : Br : NO_2 : Br = 1 : 2 : 4 : 6]$ . In order to remove all doubt as to its identity, it was converted into nitrodibromaniline by the action of alcoholic ammonia at  $180^\circ$ ; the product melted at  $202^\circ$  to  $203^\circ$ , and agreed in all its properties with Koerner's derivative  $[NH_2 : Br : NO_2 : Br = 1 : 2 : 4 : 6]$  (*Gazzetta*, 4, 369, *et seq.*). From these results it is certain that the dibromanisic acid,  $C_6Br_2(OMe).COOH$ , has the constitution  $[OMe : Br : COOH : Br = 1 : 2 : 4 : 6]$ , and it follows also that the dibromhydroxybenzoic acid mentioned in the former paper (*loc. cit.*) has a similar constitution.

C. E. G.

**Substituted Aromatic  $\beta$ -Lactones and Derivatives of Cinnamic Acid.** By A. BASLER (*Ber.*, 17, 1494—1503).—This paper forms a continuation of the author's previous communication on this subject (this vol., 603).

When ammonia in excess is allowed to act on paranitrophenyl- $\beta$ -bromopropionic acid or its lactone in the presence of water, *paranitrophenyl- $\beta$ -alanine*,  $C_9H_{10}N_2O_4$ , is formed. This body crystallises in small white scales or prisms which melt at  $166$ — $167^\circ$ . It is *very* sparingly soluble in the usual solvents in the cold, more easily in boiling alcohol and water, and in glacial acetic acid. It dissolves in a hot solution of sodium carbonate, but crystallises out unchanged on cooling. A hot aqueous solution dissolves mercuric oxide yielding

long colourless needles, from which the alanine is regenerated by acids. When diazotised, it yields nitrophenyllactic acid. It does not form metallic salts, but yields a hydrochloride crystallising in small needles, and a hydrobromide forming colourless plates or cubes melting at 132—135°; both these salts are decomposed by water. Acids and alkalis decompose it into ammonia and paranitrophenyllactic acid: but if dissolved in concentrated sulphuric acid, it yields a body crystallising in white needles which melt at 180°. When heated with acetic anhydride, it yields a monacetyl-derivative, which crystallises in small colourless scales, fuses at 140—150°; and is soluble in alcohol, ether, and glacial acetic acid, but insoluble in a solution of sodium carbonate.

When paranitrophenyl- $\beta$ -bromopropionic acid is acted on by aniline in the cold, an aniline salt of the acid is obtained, from which the acid is regenerated by acetic or other acid. When aniline is used in large excess, and the mixture is digested at 100°, *paranitrophenyl- $\beta$ -anilidopropionic acid*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{COOH}$ , is obtained. It is also formed when the aniline salt described above is dissolved in an alkali. It crystallises in yellow prisms which melt at 120—122°, and are soluble in alcohol and benzene, sparingly so in boiling water or acetic acid. It forms yellow metallic salts—of which the *ammonium salt* is the most characteristic and crystallises in yellow silky needles melting at 150—156°—whilst with mineral acids it yields crystallisable salts which are decomposed by water. By etherifying the yellow acid, the same ethyl salt is obtained as is formed by the action of aniline on the ether of the brominated acid; it crystallises in cubes which are sparingly soluble in the usual solvents. It forms no salts with acids. With paranitrophenyl- $\beta$ -propiolactone, aniline yields paranitrophenyl- $\beta$ -lactanilide which melts at 176—178°, and in its general characteristics very much resembles the  $\beta$ -alanine described above.

Taking all these data into consideration, the author believes this  $\beta$ -alanine to be paranitrophenyl- $\beta$ -lactamide,

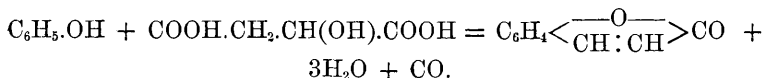


and the  $\beta$ -alanine described by Einhorn (this vol., 304) to be the corresponding ortho-compound, and not, as that investigator supposed, an internal anhydride. The author believes that its formation from the brominated acid is probably preceded by that of the lactone.

L. T. T.

**New Mode of Formation of the Coumarins; Synthesis of Daphnetin.** By H. v. PECHMANN (*Ber.*, 17, 929—936).—The only known method of preparing the coumarins synthetically is to apply Perkin's reaction to the hydroxyaldehydes; this method has been successfully employed by Perkin, Tiemann, and Kauffmann, but the preparation of the hydroxyaldehydes often offers very great difficulties. The synthesis of these compounds is of special interest, as probably very many vegetable products belong to this class—among others, *æsculetin* and *daphnetin*. By allowing concentrated sulphuric acid, zinc chloride, or other similar dehydrating agents to act at high temperatures on a mixture of a phenol and malic acid, water and carbonic

oxide are eliminated, and a coumarin is formed more or less easily according to the nature of the phenol employed. Thus in the case of coumarin,



This reaction really takes place in three stages :—(1.) The conversion of the malic acid into the hypothetical half-aldehyde of malonic acid and formic acid, which is decomposed into water and carbon monoxide,  $\text{COOH}.\text{CH}(\text{OH}).\text{CH}_2.\text{COOH} = \text{CH}_2\text{O} + \text{CHO}.\text{CH}_2.\text{COOH}$ . This reaction resembles the conversion of lactic acid into formic acid and acetaldehyde, and is proved by the formation of a condensation-product,  $\text{C}_6\text{H}_5\text{O}_4$ , of the half-aldehyde of malonic acid (see p. 1124). (2.) The union of the nascent aldehyde with the phenol to form an ortho-hydroxyphenyl-lactic acid,  $\text{C}_6\text{H}_5.\text{OH} + \text{CHO}.\text{CH}_2.\text{COOH} = \text{OH}.\text{C}_6\text{H}_4.\text{CH}(\text{OH}).\text{CH}_2.\text{COOH}$ . (3.) The elimination of 2 mols. of water,  $\text{OH}.\text{C}_6\text{H}_4.\text{CH}(\text{OH}).\text{CH}_2.\text{COOH} = \text{C}_6\text{H}_4\langle\overset{\text{O}}{\text{C}_2\text{H}_2}\rangle\text{CO} + 2\text{H}_2\text{O}$ .

The second stage quite corresponds with the method of v. Pechmann and C. Duisberg (this vol., 66) for the preparation of coumarins, and the author considers these two methods of synthesis as sufficient proof against the objections of Wittenberg and of Michael (this vol., 736). This reaction also explains Schmid's synthesis of methylumbelliferone, and is capable of great extension, since other hydroxy-acids of the fatty series may be employed, and the phenols may be replaced by aromatic amido-compounds.

Thus far, the actions of phenol, resorcinol, and pyrogallol on malic acid have been examined. Phenol acts with difficulty, forming coumarin in small quantity; the other two yield umbelliferone and daphnetin respectively.

*Umbelliferone*,  $\text{OH}.\text{C}_6\text{H}_3\langle\overset{\text{O}}{\text{CH}:\text{CH}}\rangle\text{CO}$  [ $\text{OH}:\text{O}:\text{CH} = 1:3:4$ ].

—Resorcinol and malic acid in molecular proportion are heated with twice their weight of strong sulphuric acid, then poured into iced water, and after a time the crystalline mass is collected and recrystallised.

*Daphnetin*,

$(\text{OH})_2\text{C}_6\text{H}_2\langle\overset{\text{O}}{\text{CH}:\text{CH}}\rangle\text{CO}$  [ $\text{OH}:\text{OH}:\text{O}:\text{CH} = [1:2:3:4]$ ].

—The preparation is carried out as in the preceding case; it gives all the reactions of natural daphnetin, whose constitution was first made out by Stünkel, but he failed to prove the presence of more than one hydroxyl-group, that is, he could only prepare a monacetyl-derivative and a monobenzoyl-derivative. The author has, however, prepared *diacetyldaphnetin* from both natural and artificial daphnetin; it melts at 129; and also *dibenzoyldaphnetin* which crystallises in needles and melts at 152°.

H. B.

**$\beta$ -Lactone of Metanitrophenyl-lactic Acid.** By G. PRAUSNITZ (*Ber.*, 17, 595—599).—The starting point in the preparation of this

compound was metanitrocinnamic acid, prepared from metanitrobenzaldehyde by Perkin's reaction; this acid was next heated at  $100^{\circ}$  in sealed tubes with glacial acetic acid, saturated with hydrobromic acid. In this way *metanitrophenylbromopropionic acid* is prepared, which is sparingly soluble in boiling toluene and light petroleum, more easily in benzene, and very soluble in glacial acetic acid, chloroform, ether, and absolute alcohol. When boiled with water, it yields *metanitrostyrolene*, *nitrocinnamic* and *nitrophenyl-lactic acids*, these compounds are also formed by boiling it with solution of sodium carbonate sufficient for neutralisation; when treated with an excess of caustic alkali *metanitrocinnamic acid* is obtained.

*$\beta$ -Lactone of metanitrophenyl-lactic acid*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}<\underset{\text{O}}{\text{CH}_2}>\text{CO}$ , is obtained by neutralising the above acid carefully with a solution of sodium carbonate in the cold, and allowing the solution to remain some hours, when a crystalline mass separates out which, after solution in benzene and precipitation with light petroleum, is obtained in small white crystals melting at  $98^{\circ}$ ; when heated above its melting point, it is resolved into carbonic anhydride and nitrostyrolene.

*Metanitrostyrolene*,  $\text{C}_8\text{H}_7\cdot\text{NO}_2$ , is best obtained by boiling the nitro-bromopropionic acid with sodium carbonate, when it passes over with the steam; it may be extracted from the distillate by ether. On evaporation, the ethereal solution leaves an oil which solidifies at  $-15^{\circ}$ . It is easily soluble in ether, alcohol, light petroleum, chloroform, and glacial acetic acid.

*Metanitrostyrolene dibromide*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$ , is obtained by adding bromine to a solution of nitrostyrolene in glacial acetic acid; it crystallises from alcohol in well-formed crystals melting at  $78-79^{\circ}$ .

*Metanitrophenyl- $\beta$ -lactic acid*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{COOH}$ , is formed, together with nitrocinnamic acid and nitrostyrolene, as described above. It is separated from the nitrocinnamic acid by its solubility in water, the mother-liquors from this acid yielding the phenyl-lactic acid on extraction with ether. Nitrophenyl-lactic acid crystallises from water in white lustrous leaflets which melt at  $105^{\circ}$ . When it is heated at  $140^{\circ}$  in sealed tubes with glacial acetic acid, which has been saturated with hydrobromic acid, nitrophenylbromopropionic acid is reproduced.

P. P. B.

**Hydroxyphenylacetic Acids.** By H. SALKOWSKI (*Ber.*, 17, 504—510).—In the preparation of these compounds, the author first obtains the three isomeric nitrobenzyl cyanides by nitrating benzyl cyanide and separating these by systematic crystallisation from glacial acetic acid. Besides the para-, ortho-, and meta-nitrobenzyl cyanides, a fourth body is formed, identical with that described by Perkin (*Trans.*, 1883, 112), but which is not the ortho-derivative as was supposed by Perkin.

*Parahydroxybenzyl cyanide*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CN}$ , is obtained by treating an acid solution of the amido-derivative with sodium nitrite; it crystallises from hot aqueous solutions in large shining tables, which melt at  $69-70^{\circ}$ . Its aqueous solution yields a violet coloration with

ferrie chloride. On saponification with hydrochloric acid, it yields *parahydroxyphenylacetic acid*, melting at  $148^{\circ}$ . The cyanide, when heated with potassium hydroxide and methyl iodide, yields a methyl ether, which, by saponification with hydrochloric acid, is converted into *paramethoxyphenylacetic acid*, an acid homologous with anisic acid.

*Metanitrobenzyl cyanide* forms large well-defined monoclinic crystals melting at  $61^{\circ}$ . The author finds that the corresponding phenylacetic acid melts at  $120^{\circ}$ , somewhat higher than the melting point given by Gabriel and Borgmann (Abstr., 1883, 1121). *Metamidobenzyl cyanide* is an oily liquid, which was converted into the hydroxy-derivative, a substance easily soluble in alcohol, ether, and water, and crystallising on slow evaporation of its aqueous solution in rhombic tables melting at  $52-58^{\circ}$ . *Metahydroxyphenylacetic acid* was obtained by saponification of the cyanide, it crystallises from hot benzene or light petroleum in slender needles, which melt at  $129^{\circ}$ . Ferric chloride gives with its aqueous solutions at first a violet coloration, but it rapidly fades.

*Orthonitrobenzyl cyanide* crystallises in large well-defined rhombic prisms melting at  $84^{\circ}$ ; it yields the nitrophenylacetic acid melting at  $141^{\circ}$  (Bedson, Trans., 1880, 90). The author has not succeeded in isolating in a state of purity the corresponding amidobenzyl cyanide, the crude amido-derivative treated with sodium nitrite, &c., does not yield an hydroxy-derivative, but a compound crystallising in slender colourless needles, melting at  $139^{\circ}$ , and apparently of the composition  $C_8H_6N_2O$ . This, when heated with hydrochloric acid, does not yield hydroxyphenylacetic acid, but a compound,  $C_{14}H_{11}N_3O_4$ , melting at  $254^{\circ}$ .  
P. P. B.

**Condensation-products from Phthalic Anhydride.** By S. GABRIEL (*Ber.*, 17, 1389—1396).—The author has previously shown (Abstr., 1881, 733) that by heating phthalic anhydride with ethyl acetate and sodium acetate there was obtained orthotribenzoylene benzene and a crystalline substance, to which he provisionally assigned the formula  $C_{12}H_8O_2$ . This formula should be doubled. On nitration, the substance yields a nitro-derivative,  $C_{24}H_{14}(NO_2)_2$ , crystallising in groups of slender needles, melting at over  $280^{\circ}$ , soluble in boiling nitrobenzene, sparingly soluble in boiling glacial acetic acid. By heating it with hydriodic acid and phosphorus for three hours at  $170-175^{\circ}$ , it is converted into a new hydrocarbon, phthalacene,  $C_{24}H_{16}$ , ethyl iodide, and carbonic anhydride. *Phthalacene* forms long colourless crystals, and melts at  $173^{\circ}$ . Its derivatives are described in the Abstract, p. 1189. From these results, it seemed highly probable that the compound,  $C_{24}H_{16}O_4$ , was the ethyl salt of an acid,  $C_{21}H_{11}O_2.COOH$ , phthalaconecarboxylic acid, and further investigation has completely confirmed this view.

By heating the compound,  $C_{24}H_{16}O_4$ , with concentrated sulphuric acid for half an hour, and pouring the blood-red liquid into water, a citron-yellow precipitate is obtained, which may be purified by crystallisation, first from boiling alcohol, then from boiling glacial acetic acid, and again several times from boiling alcohol; on mixing the hot alcoholic solution with hot alcoholic potash, *potassium*

*phthalaconecarboxylate*,  $C_{21}H_{11}O_2.COOK + H_2O$ , separates in slender yellow needles. The sodium salt,  $C_{21}H_{11}O_2.COONa + H_2O$ , crystallises in slender golden-yellow needles.

*Phthalaconecarboxylic acid*,  $C_{21}H_{11}O_2.COOH$ , obtained by decomposing the alkali salts with hydrochloric acid, crystallises in yellow microscopic needles, melts at  $280-281.5^\circ$ , is moderately soluble in hot alcohol, less soluble in hot glacial acetic acid.

*Ethyl hydrophthalaconecarboxylate*,  $C_{21}H_{13}(OH)_2.COOEt$ , prepared by the action of zinc-dust on a solution of ethyl phthalaconecarboxylate in boiling glacial acetic acid, forms a very pale-yellow crystalline powder, which melts at  $211-213^\circ$ . When heated with potash, it is converted into a dark resin, which on digestion with hot water, gives an indigo-blue solution, whilst yellow crystals remain undissolved.

*Hydrophthalaconecarboxylic acid*,  $C_{21}H_{13}(OH)_2.COOH$ , obtained by the action of zinc in alkaline solution of phthalaconecarboxylic acid, crystallises in colourless microscopic needles, and melts at over  $280^\circ$ . It was not obtained in a state of purity.

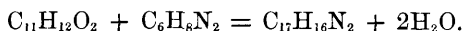
*Ethyl dioximidophthalacenecarboxylate*,  $C_{21}H_{11}(NOH)_2.COOEt$ , prepared by the action of hydroxylamine hydrochloride on ethyl phthalaconecarboxylate, crystallises in yellow needles, and melts at  $263-264^\circ$ .

*Dioximidophthalacenecarboxylic acid*,  $C_{21}H_{11}(NOH)_2.COOH$ , forms brownish-yellow needles, melts with decomposition at  $271-273^\circ$ , is readily soluble in alcohol, sparingly soluble in glacial acetic acid.

On repeating his experiments with phthalic anhydride and ethyl malonate, the author has not been able to obtain again the substance crystallising in needles melting at  $217-219.5^\circ$ . A. J. G.

**$\alpha$ -Hydroxyphthalic Acid.** By O. MILLER (*Ber.*, 17, 552).—The author claims priority in the discovery of the acid described by Jacobsen as  $\beta$ -hydroxyorthophthalic acid (*Abstr.*, 1883, 1224), which had been already obtained by him and described with other derivatives of phthalic acid (*Abstr.*, 1882, 404). P. P. B.

**Derivatives of the Ethereal Salts of Acetophenoneacetoacetic Acid.** By C. PAAL (*Ber.*, 17, 913-918).—(*Comp.* this vol., 598 and 746.) By the action of dilute hydrochloric acid on ethyl acetophenoneacetoacetate, Weltner (this vol., 746) obtained a body having the same composition as acetophenoneacetone, but it differs essentially from acetophenoneacetone, as described by the author. By the action of excess of phenylhydrazine, it yields a crystalline mass which, after purification by crystallisation from benzene and alcohol, melts at  $154-155^\circ$ , and has the composition  $C_{17}H_{16}N_2$ :—



When acetophenoneacetone is heated with dehydrating agents, such as acetic anhydride, then neutralised with potash and distilled with steam, it yields a crystalline body,  $C_{11}H_{10}O$ , insoluble in water and alkalis; this melts at  $41-42^\circ$ , and boils at  $235-240^\circ$ . Its constitution is not determined. It does not form additive-products with



bromine, and on oxidation it yields benzoic acid. Another body, isomeric with the preceding, is formed at the same time, it is less volatile and cannot be distilled without decomposition, it melts at 82—83°, combines directly with bromine, and is converted into the above-described body,  $C_{17}H_{16}N_2$ , by the action of phenylhydrazine.

The formation of the acid,  $C_{12}H_{10}O_3$ , has been previously described. When treated with potassium permanganate, it yields benzoic, acetic, and carbonic acids; hydriodic acid and phosphorus convert it into a hydrocarbon, probably  $C_{11}H_{14}$ . The potassium salt of the acid crystallises from alcohol anhydrous, and from water, with water of crystallisation; the ammonium salt is anhydrous, and scarcely soluble in aqueous ammonia. Hydrochloric acid passed into the alcoholic solution of the acid gives rise to the formation of an oil,  $C_{12}H_{10}O_3Et$ . The author, in continuing the work, hopes to show some connection between these compounds and naphthalene.

H. B.

**Acetylation of Gallic Acid and Tannin.** By C. BÖTTINGER (*Ber.*, **17**, 1503—1507).—When hydrated gallic acid is gently warmed with excess of acetic anhydride, it yields *triacetogallic acid*, but if the gallic acid is first dehydrated, the triaceto-compound is mixed with a *pentacetyl-compound* melting at 151°, and somewhat resembling pentacetotannic acid in properties. Crystallised tannic acid, when treated with cold acetic anhydride, yields *pentacetotannic acid*.

The author has investigated the action of acetic anhydride on the aqueous extracts of *divi-divi*, *algarroilla*, *valonia*, and *nutgall*. The principal constituent of the acetyl-derivatives appeared in each case to be a substance of the composition of triacetogallic acid, but isomeric and not identical with this latter.

L. T. T.

**Digallic Acid.** By C. BÖTTINGER (*Ber.*, **17**, 1475—1479).—The author finds that the derivatives of gallic acid previously described by him (this vol., 55) do not contain the pyruvic nucleus, and that the pyruvic acid used in the reaction may be replaced by glyoxylic acid without change of products. If, however, it is replaced by acetic acid, the gallic acid undergoes scarcely any change (only a trace of rufigallic acid being formed), whereas if no foreign acid be employed, the whole of the gallic acid will be converted into rufigallic acid.

Gallic acid or ether is moistened with pyruvic or glyoxylic acid, concentrated sulphuric acid added, and the whole heated for half an hour in the water-oven. A substance is thus formed which is easily soluble in water, and somewhat resembles in properties the body described by Schiff (this Journal, 1874, 267). If the heating with sulphuric acid is continued for several hours, a substance is obtained which is insoluble in water, but soluble in acetic anhydride with formation of an acetyl-derivative. The soluble substance is very hygroscopic, has a strong odour, and melts below 100°, giving off water, but undergoing little further change until about 148°, when it is converted into an insoluble substance. Its formula is  $C_{14}H_{14}O_{11}$ , but when dried at a little above 100°, it loses 2 mols.  $H_2O$ , but at the same time is slightly decomposed. The dried body, when digested

with acetic anhydride at  $100^{\circ}$ , yields a pentacetyl-derivative of the formula  $C_{14}H_6Ac_5O_9$ , so that the acid must be  $C_{14}H_{10}O_9 + 2H_2O$ . The author calls the substance *digallic acid*, and believes the insoluble substance to be its anhydride. Digallic acid is isomeric but probably not identical with tannin.  
L. T. T.

**Morin.** Part I. By R. BENEDIKT and K. HAZURA (*Monatsh. Chem.*, 5, 165—176).—A short notice of these results has already appeared (this vol., 846). The dyeing properties of fustic (*Morus tinctoria*) are usually attributed to the presence of two substances, morin and maclurin. This would appear, however, to be in part erroneous, as from many of the commercial extracts not even a trace of these substances can be obtained, although yielding good results in dyeing. Experiments of Klaye show that maclurin is not a dye, as it only gives a very pale dirty yellowish-brown colour on goods mordanted with alumina; pure morin, on the contrary, gives intense pure yellows.

Morin is best prepared as follows:—20 kilos. of fustic extract of  $20^{\circ}$  Baume is well mixed with an equal volume of water and a little hydrochloric acid, the clear liquid decanted, and the residue repeatedly treated with acidulated water in similar manner, until the washings are no longer yellow. The residue is then pressed, powdered, and air-dried. The crude morin so obtained is dissolved in alcohol by aid of heat, and one-tenth of the volume of hot water added; on cooling, pure morin separates. The filtrate is again heated to boiling and a small quantity of hot water added, when more morin separates. This is repeated on the filtrate until the last addition of hot water causes no separation. The various crystallisations are then mixed together and recrystallised in a similar manner.

By fusing morin with potash, Hlasiwetz and Pfaundler (*J. pr. Chem.*, 94, 65) obtained phloroglucinol alone, and, in some experiments, a little oxalic acid. The authors find that resorcinol is also formed in large quantity.

By reducing morin with sodium amalgam, phloroglucinol is obtained, and also an acid which yields resorcinol on distillation, and therefore must stand in some simple relation to it. According to Hlasiwetz and Pfaundler (*loc. cit.*) phloroglucinol alone is formed. The yield of phloroglucinol obtained by the authors was less than one-ninth of that required on the theory of its being the only product. The authors have failed to obtain the isomorphin of Hlasiwetz and Pfaundler; they can at present assign no reason for their want of success.

The oxidation of morin with nitric acid yields styphnic acid (trinitroresorcinol), according to Wagner (*J. pr. Chem.*, 51, 82). Hlasiwetz and Pfaundler found oxalic acid to be the usual product of the action of oxidising agents on morin. By the careful oxidation of morin dissolved in glacial acetic acid with nitric acid, the authors have obtained  $\beta$ -resorcylic acid, and another substance separating, on addition of baryta to the reaction-product, as a voluminous greyish-brown precipitate; small quantities of oxalic acid and of a nitro-product were also observed.

From a consideration of all the analyses yet published, the authors arrive at the conclusion that morin is best represented by the formula  $C_{12}H_8O_6$  for the dried substance. It crystallises with 1 mol.  $H_2O$ .

From the foregoing results, it follows that morin must have a constitution analogous to that of maclurin, as they are both resolved by simple reactions into phloroglucinol and an acid of the formula  $C_7H_6O_4$ ; protocatechuic acid in the case of maclurin, and  $\beta$ -resorcylic acid in that of morin.

A. J. G.

**Derivatives of Benzenesulphonic Acid.** By R. HÜBNER (*Annalen*, **223**, 234—246).—The ethereal salts of benzenesulphonic acid are obtained by the action of benzenesulphonic chloride on dry sodium methylate, ethylate, &c., suspended in absolute ether. The ethylic salt which has been previously described by Schiller and Otto (*Ber.*, **9**, 1638) has the sp. gr. 1.22 at 17°. The methyl and propyl salts resemble this substance in their properties. Their specific gravities at 17° are 1.272 and 1.1785 respectively. Negative results were obtained in attempts to prepare the anhydride of benzenesulphonic acid by the action of benzenesulphonic chloride on benzenesulphonic acid or on the sodium, ethyl, or silver salt of the acid.

W. C. W.

**Nitro- and Amido-triphenylphosphine Oxide.** By A. MICHAELIS and H. v. SODEN (*Ber.*, **17**, 921—924).—Fuming nitric acid dissolves triphenylphosphine, and on pouring the solution into water, a mixture of triphenylphosphine nitrate,  $Ph_3P(NO_3)_2$ , and triphenylphosphine hydroxide,  $Ph_3P(OH)_2$ , is deposited as an oil; on exposure to the air, it is entirely converted into the latter. By evaporating the nitric acid solution to dryness, the nitrate is obtained purer; but by long standing over slaked lime and sulphuric acid, it leaves a basic nitrate,  $Ph_3P(NO_3)(OH)$ . By employing a mixture of nitric and sulphuric acids, substitution and oxidation take place. The hydroxide is best prepared by treating triphenylphosphine first with water and bromine, then with caustic soda; when heated, it loses water and leaves the oxide,  $Ph_3PO$ , boiling above 360°. When the hydroxide is dissolved in cold nitric and sulphuric acids and the solution poured into water, it yields a precipitate of *trinitrotriphenylphosphine oxide*; it melts at 243°.

*Triamidotriphenylphosphine oxide* is obtained by reduction of the preceding body with tin and hydrochloric acid. It is only slightly soluble in cold water, melts at 259°, and its salts are very soluble. Dissolved in acetic anhydride and precipitated with ether, it yields the acetyl-derivative,  $(NHAc.C_6H_4)_3PO + H_2O$ , melting at 187.5°. The benzoyl-derivative,  $(NH\bar{B}z.C_6H_4)_3PO$ , melts at 180°. Bromine added to the solution of the hydrochloride produces a precipitate, probably  $(NH_2.C_6H_4Br_2)_3PO$ . The base is isomeric with Schiff's anilide of orthophosphoric acid,  $PO(NHPh)_3$ .

H. B.

**Synthesis of Indole-derivatives.** By E. FISCHER and O. HESS (*Ber.*, **17**, 559—568).—One of the authors has already shown (this vol., 52) that methylphenylhydrazine and pyrroacemic acid unite together to form an acid, which when treated with hydrochloric

acid, is resolved into ammonia, and an acid,  $C_{10}H_9NO_2$ . The further investigation of this compound shows that it is related to indole, into a methylated derivative of which it is converted by heat, and therefore the authors style this acid *methylindolecarboxylic acid*.

*Methylindole*,  $C_9H_7N$ , obtained by heating the above acid at  $205^\circ$ , is a yellow oil, volatile in steam, and boils at  $239^\circ$ ; it is insoluble in water, but easily miscible with alcohol, ether, and benzene. In physical and chemical properties, it exhibits a great resemblance to indole; with pine wood moistened with hydrochloric acid, it gives a violet coloration. Methylindole and picric acid unite to form a *picrate*,  $C_9H_7N \cdot C_6H_2(NO_2)_3.OH$ , crystallising from ether in dark red prisms, melting at  $150^\circ$ .

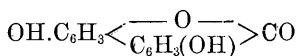
*Methylpseudisatin*,  $C_9H_7NO_2$ .—If methylindole is treated with solutions of sodic hypobromite or hypochlorite, a halogen-derivative is formed, the bromine or chlorine of which is easily substituted, and when the compound is treated with alcoholic soda *methylpseudisatin* is produced. This crystallises from water in beautiful red needles, melting at  $134^\circ$ ; its properties are similar to those of Baeyer's ethylpseudisatin (*Ber.*, **16**, 2193); it yields an indophenine with coal-tar benzene and sulphuric acid, and like isatin unites directly with phenylhydrazine.

Ethylphenylhydrazine unites directly with pyrrocemic acid, forming ethylphenylhydrazine-pyrrocemic acid, which when heated with hydrochloric acid yields *ethylindolecarboxylic acid*,  $C_{11}H_{11}NO_2$ , crystallising in colourless needles which melt at  $183^\circ$ . Like the methyl-derivative, it is resolved by heat into carbonic anhydride and *ethylindole*,  $C_{10}H_{11}N$ , a liquid boiling  $8^\circ$  higher than methylindole, to which it has the closest resemblance. Ethylindole is oxidised by sodic hypochlorite, and converted into *ethylpseudisatin*, identical with that described by Baeyer (*loc. cit.*).

Diphenylhydrazine and pyrrocemic acid unite to form *diphenylhydrazinepyrrocemic acid*,  $NPh_2.N : CMe.COOH$ , which crystallises from hot alcohol in white needles, melting at  $145^\circ$ ; when heated with hydrochloric acid, it is converted into *phenylindolecarboxylic acid*, crystallising from alcohol in white needles, melting at  $173$ – $176^\circ$ ; this when heated at  $200$ – $210^\circ$  loses carbonic anhydride, and yields a heavy oil, apparently phenylindole. P. P. B.

**New Reaction of Benzidine.** By P. JULIUS (*Monatsh. Chem.*, **5**, 193–194).—In aqueous solutions of benzidine, potassium dichromate produces a voluminous precipitate of interlaced blue needles of benzidine chromate,  $C_{12}H_8(NH_2)_2.H_2CrO_4$ . It is insoluble in the ordinary solvents, and is partially decomposed on boiling with water; when boiled with dilute ammonia, it is converted into benzidine, ammonium dichromate, and a brownish amorphous substance, containing much chromium. The reaction is sensitive, as a solution containing 1 part of benzidine in 5000 parts water gives a distinct precipitate on heating. The isomeric diphenylene gives a similarly delicate reaction with potassium dichromate. A. J. G.

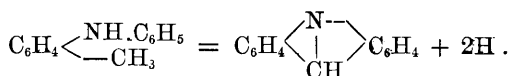
**The Euxanthone Group.** By E. SPIEGLER (*Monatsh. Chem.*, **5**, 195—202; and *Ber.*, **17**, 807—810).—Diphenylene ketone when treated with hydroxylamine hydrochloride and alcohol, yields *diphenyleneacetoxime*,  $\langle \text{C}_6\text{H}_4 \rangle \text{C} : \text{NOH}$ , forming pale yellow crystals, and melting at  $192^\circ$ . All attempts to convert diphenylene ketone oxide and euxanthone into the corresponding oximes, either by treatment with free hydroxylamine or its hydrochloride, were unavailing. These negative results appear to throw considerable doubt on the accuracy of the formulæ  $\text{O} \langle \text{C}_6\text{H}_4 \rangle \text{CO}$  and  $\text{O} \langle \text{C}_6\text{H}_3(\text{OH}) \rangle \text{CO}$ , usually assigned to these bodies. The absence of the ketone-group is further confirmed by their not reacting with phenylhydrazine. The author considers it probable that they may be lactones, and suggests the formulæ  $\text{C}_6\text{H}_4 \langle \text{O} \rangle \text{CO}$  for diphenylene ketone oxide, and



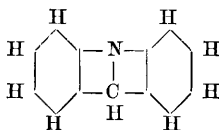
for euxanthone. It has been already shown that  $\alpha$ - and  $\gamma$ -lactones do not react with hydroxylamine, and the author now shows that coumarine, a  $\Delta$ -lactone,  $\text{C}_6\text{H}_4 \langle \text{O} \rangle \text{CO}$ , is also without action.

Paradioxybenzophenone, treated with hydroxylamine and alcohol, readily yields the corresponding *oxime*,  $\text{C}(\text{C}_6\text{H}_4\text{OH})_2 : \text{NOH}$ , as a yellow oil, crystallising on long standing. This result shows that the presence of other oxygen-atoms in the molecule does not prevent the ketone-group reacting with hydrogen. That a high molecular weight does not prevent the reaction is shown by the formation of *phenyl- $\alpha$ -naphthylacetoxime*, by the action of phenyl- $\alpha$ -naphthyl ketone on hydroxylamine. It forms a yellow oil of the formula  $\text{C}_{10}\text{H}_7\text{CPh} : \text{NOH}$ .  
A. J. G.

**Formation of Acridine.** By C. GRAEBE (*Ber.*, **17**, 1370—1371).—The synthesis of acridine from diphenylamine leads to the view that its constitution is analogous to that of anthracene, and not to that of phenanthrene. A still further confirmation of this assumption is now brought forward by the author, who shows that a large yield of acridine is obtained by passing orthotolylaniline through a red-hot tube, the reaction being expressed by the equation

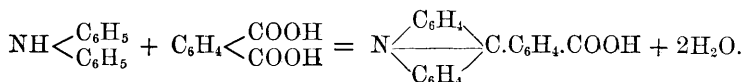


Benzylidene-aniline does not yield acridine when passed through a red-hot tube, whilst it should do so if acridine had a constitution similar to that of phenanthrene. Orthoditolylaniline yields acridine, and a methylated acridine. Paratolylaniline does not yield acridine at a red heat. These experiments give further proof that the nitrogen and CH-group are in the ortho-position in both benzene-groups, the constitution of acridine being expressed by the formula



A. J. G.

**Butylacridine and Acridylbenzoic Acid.** By A. BERNTHSEN and J. TRAUBE (*Ber.*, **17**, 1508—1512).—*Butylacridine*,  $C_{17}H_{17}N$ , was obtained by heating a mixture of valeric acid and diphenylamine with zinc chloride for 20 hours at 200—220°. It forms a white amorphous substance, which rapidly turns brown when exposed to the air. It distils without much decomposition. Its *hydrochloride* crystallises in brownish-yellow rhombohedral prisms which melt at 191°; in dilute alcoholic solution, it exhibits a strong bluish-green fluorescence. The *nitrate* forms long, pale yellow, silky needles, melting at 139°; the *chromate*  $C_{17}H_{17}N, H_2CrO_4$ , crystallises in orange needles, which melt at a little above 100°, with evolution of acridine. Reduced with zinc, the hydrochloride yields *hydrobutylacridine*,  $C_{17}H_{19}N$ , which forms glittering white scales melting at 90—92°. *Acridylbenzoic acid*,  $C_{13}H_9N.C_6H_4.COOH$ , is obtained by heating phthalic anhydride and diphenylamine with zinc chloride at 180—200° for about 12 hours. It crystallises in yellow prisms or needles, easily soluble in dilute acids or alkalis, almost insoluble in boiling water. Its dilute solutions in acids have a green, and in alkaline solution, a blue fluorescence. It may be heated to 300° without change, but above that temperature it is decomposed with evolution of phenylacridine. Its *hydrochloride* crystallises in small yellow needles or tables, which melt at 163°. Its *sodium salt* crystallises in mother-of-pearl-like scales or needles, which are very soluble in water, and contain water of crystallisation (probably  $1\frac{1}{2}$  mols.). The *silver salt* is yellowish-white and amorphous; the *copper-salt* bluish-green. By reduction, *hydroacridylbenzoic acid*,  $C_{20}H_{16}NO_2$ , is obtained in the form of colourless needles, which readily become reoxidised to acridylbenzoic acid. Like other hydroacridines it has no basic properties. The formation of acridylbenzoic acid is probably explained by the equation—



L. T. T.

**New Method of Preparing Carbostyryl.** By J. ROTHEIT (*J. pr. Chem.* [2], **29**, 300—302).—This is a preliminary note on the formation of carbostyryl by heating trichloroxyquinoline with fuming hydriodic acid in a sealed tube at 250°. The trichloroxyquinoline was prepared by acting with chlorine on a solution of quinoline in dilute acetic acid, first in the cold, and then with the aid of heat. P. F. F.

**$\alpha$ - and  $\beta$ -Methylnaphthalene.** By K. E. SCHULZE (*Ber.*, **17**, 842—846).—Fittig prepared  $\alpha$ -methylnaphthalene from  $\alpha$ -bromonaphthalene and methyl iodide; Reingruber (*Abstr.*, 1881, 436) isolated a

substance from coal-tar which he believed to be different from Fittig's product, and called  $\beta$ -methylnaphthalene.

A sample of coal-tar oil purified by sulphuric acid and caustic soda and boiling at 200—300° was examined. By fractionation an oil boiling at 139—142° and solidifying at 2°, was isolated; this after repeated melting and recrystallisation and pressing, followed by crystallisation from alcohol, melted constantly at 32·5°. Analysis showed it to be methylnaphthalene; it boils at 241—242°. The author considers this to be  $\beta$ -methylnaphthalene, and Reingruber's and Fittig's products to have been essentially the same. The following compounds have been obtained pure: the *picrate*, crystallising from alcohol and melting at 115°:  $\alpha$ -nitro- $\beta$ -methylnaphthalene, melting at 81°, is formed together with a small quantity of a dinitro-derivative melting at 206° by the action of a mixture of nitric and sulphuric acids on  $\beta$ -methylnaphthalene.

The oil pressed from the  $\beta$ -methylnaphthalene, and which did not crystallise at -15°, was purified and found to be a methylnaphthalene: it boils at 240—243°; according to Fittig the boiling point of  $\alpha$ -methylnaphthalene is 231—232°, the author, however, has made a preparation according to Fittig's directions, and found the boiling point to be also 240—242°. The mononitro-substitution product is an oil not crystallising at -15°; the *picrate* melts at 116°. Reingruber could prepare neither a crystalline nitro-derivative nor a *picrate*; his product was neither  $\beta$ - nor pure  $\alpha$ -methylnaphthalene. H. B.

$\alpha$ - and  $\beta$ -Methylnaphthalene. By K. E. SCHULZE (*Ber.*, 17, 1527—1530).—*Esobromo- $\alpha$ -methylnaphthalene* (for nomenclature see this vol., 998) was obtained by exposing a mixture of molecular proportions of  $\alpha$ -methylnaphthalene and bromine dissolved in carbon bisulphide to the action of sunlight. It was purified by the help of its picric acid compound. It is a colourless liquid with a slight odour resembling that of bromotoluene, and boiling with slight decomposition at 298°, corr. It forms a compound with picric acid which crystallises in deep yellow needles melting at 105°. *Esobromo- $\beta$ -methylnaphthalene*, prepared in a similar manner, boils at 296°, corr. Its picric acid compound crystallises in yellow needles melting at 113°.  $\beta$ -Naphthomethyl chloride,  $C_{10}H_7\cdot CH_2Cl$ , was obtained by passing a current of chlorine into  $\beta$ -methylnaphthalene at 240—250°. It distils at 168° under 20 mm. pressure, and solidifies to a mass of small micaceous scales. It melts at 47°, but if allowed to resolidify and *immediately* reheated it melts at 41°; if allowed to remain 15 or 20 minutes after solidification, it recovers its normal melting point of 47°.  $\beta$ -Naphthomethyl bromide was prepared in a similar manner. If the temperature during the reaction is allowed to reach 280°, total decomposition takes place. Crystallised from alcohol, it forms white fatty scales melting at 56°. It boils at 213° under 100 mm. pressure. Both the chloride and bromide resemble the corresponding benzyl-derivatives in odour. They do not form compounds with picric acid.  $\beta$ -Naphthaldehyde,  $C_{10}H_7\cdot COH$ , was prepared by oxidising the chloride or bromide with lead nitrate; it forms white scales melting at 59°, and is identical with that obtained by Battershall by the distillation

of a mixture of calcium  $\alpha$ -naphthoate and formate.  $\beta$ -Naphthoic acid is only obtained in very small quantity by the oxidation of the aldehyde, but may be prepared almost quantitatively if the chloride or bromide be oxidised by shaking with a cold solution of potassium permanganate. It melts at  $185^\circ$ , and is identical with Vieth's acid, for which he found the melting point  $182^\circ$ . L. T. T.

**Isobutylnaphthalene.** By R. WEGSCHEIDER (*Monatsh. Chem.*, 5, 236—240).—Isobutylnaphthalene is obtained by mixing 1 part of isobutyl chloride with 2 parts of fused naphthalene, and then adding aluminium chloride in small portions, the mixture being heated just sufficiently to prevent crystallisation. Excess of aluminium chloride should be avoided, about one-twelfth of the weight of the naphthalene being sufficient. In addition to isobutylnaphthalene there are formed  $\alpha$ - $\alpha$ -dinaphthyl,  $\alpha$ - $\beta$ -dinaphthyl, and isodinaphthyl: their separation can be effected by distillation with steam.

*Isobutylnaphthalene* forms a colourless oil; it boils at  $280^\circ$ , volatilises with difficulty in a current of steam, and is readily soluble in ether. The picric acid compound crystallises in aggregates of slender needles, melts at  $96^\circ$ , and is readily soluble in alcohol. Isobutylnaphthalene is not obtained by heating a mixture of naphthalene, isobutyl alcohol, and zinc chloride. A. J. G.

**Condensation-product of  $\beta$ -Naphthol with Benzaldehyde.** By W. TRZCINSKI (*Ber.*, 17, 499—501).—This condensation-product having the composition  $C_{68}H_{46}O_3$ , is obtained by treating  $\beta$ -naphthol and benzaldehyde dissolved in alcohol with concentrated sulphuric acid: by crystallisation from benzene or chloroform it is obtained in microscopic rhombic tablets melting at  $190$ — $191^\circ$ . It is insoluble in alcohol, ether, and alcoholic potash, and apparently does not contain hydroxyl-groups. It forms bromo- and chloro-substitution-products, and is converted into *melinoëintrisulphonic acid* by concentrated sulphuric acid (this vol., 590). When nitrated, it gives a compound of the composition  $C_{34}H_{17}(NO_2)_7O_2$ .

Probably the formation of this takes place in two phases: (1) a compound  $C_{34}H_{24}O_2$  is formed, thus:—



(2) 2 mols. of this condense and give  $C_{68}H_{46}O_3$ , thus:—



P. P. B.

**Naphthalene Derivatives.** By R. FLESSA (*Ber.* 17, 1479—1486).—A. J. Smith (*Trans.*, 1879, 789) showed that by the direct bromination of  $\beta$ -naphthol in acetic solution the end-product was tetra-bromonaphthol. By the use of Gustavson's method (this Journal, 1877, ii, 599), the author has obtained *pentabromo- $\beta$ -naphthol*: 2—3 grams of aluminium-foil are gradually added to a *well-cooled* solution of bromine in carbon bisulphide and then 10 grams of  $\beta$ -naphthol, the whole being finally heated to complete the reaction. When purified, pentabromo- $\beta$ -naphthol crystallises in colourless



needles which melt at  $237^{\circ}$ . It dissolves sparingly in boiling alkali, and the solution deposits the alkaline salt on cooling. When oxidised with dilute nitric acid at  $100^{\circ}$ , this substance yields *tetrabromo- $\beta$ -naphthaquinone*,  $C_{10}H_2Br_4O_2$ , which is of a red colour, crystallises in nodules, is moderately soluble in the usual solvents, and melts at  $164^{\circ}$ . Alkalis dissolve it, but not without change, as acids reprecipitate from the solution a pale-yellow substance, and the filtrate contains bromine. When heated with nitric acid of sp. gr. 1.15 in closed tubes at  $150^{\circ}$ , this quinone is converted into *tribromophthalic acid*. This substance crystallises in silky needles or scales easily soluble in ether, alcohol, acetic acid, and alkalis, moderately so in boiling water, and melts at  $190$ — $191^{\circ}$ . It forms soluble salts with alkalis: the barium salt and the calcium salt both crystallise with 2 mols.  $H_2O$ : the silver salt is precipitated as a white flocculent substance. When heated a little above its melting point, the acid is converted into *tribromophthalic anhydride*, which sublimes without decomposition in beautiful white scales melting at  $157^{\circ}$ . It is almost insoluble in cold water, and is reconverted into the acid by boiling water. It is easily soluble in the usual solvents. When fused with resorcinol, it yields a compound having properties similar to those of fluorescein.

When pentabromo- $\beta$ -naphthol is treated at  $100^{\circ}$  with bromine containing aluminium bromide, a more highly brominated derivative (probably hexabromo- $\beta$ -naphthol) is obtained; this crystallises in colourless needles, and also yields a brominated phthalic acid on oxidation. These compounds are still under investigation.

Attempts at the direct bromination of phthalic anhydride proved fruitless, even in the presence of aluminium bromide, mere traces of brominated acids being obtained.

L. T. T.

**Derivatives of Nitro- $\beta$ -naphthaquinone.** By O. KORN (*Ber.*, 17, 906—909).—Phenylazo- $\beta$ -naphthol (see this vol., 610) was converted into nitro- $\beta$ -naphthaquinone according to Stenhouse and Groves' method. Reduced with tin and hydrochloric acid the hydrochloride of *amidodihydroxynaphthulene*,  $C_{10}H_5(\alpha OH)(\beta OH)(NH_2, HCl)$ , is obtained. This base differs in several respects from the amidodihydroxynaphthol prepared by Graebe and Ludwig from biimidonaphthol; and since nitro- $\beta$ -naphthaquinone is oxidised to phthalic acid, its constitution is probably  $C_{10}H_5(OH)(OH)(NH_2)$  [ $\alpha : \beta : \beta$ ].

By the action of aniline on a boiling alcoholic solution of nitro- $\beta$ -naphthaquinone, red needles of *nitro- $\beta$ -naphthaquinoneanilide*,  $C_{10}H_4(OH)(NO_2) < \overset{O}{\underset{NPh}{\text{C}}} >$  are formed; it melts at  $253^{\circ}$ , and is insoluble in most reagents. By the continued action of aniline and alcohol, a compound is formed melting at  $183$ — $185^{\circ}$ ; alcohol alone, however, decomposes nitro- $\beta$ -naphthaquinone with the formation of a crystalline body, probably nitro- $\beta$ -naphthaquinol.

H. B.

**Note on the Chemical Constitution of Anthraquinone, Anthracene, and Analogous Compounds.** By E. v. MEYER (*J. pr. Chem.* [2], 29, 139—144).

**Constitution of Phthalic Chloride and Anthraquinone.** By V. MEYER (*Ber.*, **17**, 817—819).—The question whether phthalic chloride has the constitution  $C_6H_4(COCl)_2$  or  $C_6H_4<\begin{smallmatrix} CO \\ CCl_2 \end{smallmatrix}>O$ , is not decided by the formation of phthalophenone,  $C_6H_4<\begin{smallmatrix} -CO- \\ CPh_2 \end{smallmatrix}>O$ , but a proof that the second formula is the correct one is the fact that the so-called phthalyl ether—formed by the action of zinc ethyl on the chloride—is not a ketone, for under no conditions does it combine with hydroxylamine; it is probably a lactone,  $C_6H_4<\begin{smallmatrix} -CO- \\ CEt_2 \end{smallmatrix}>O$ .

E. v. Meyer (*J. pr. Chem.* [2], **29**, 139) has supposed that anthraquinone is a lactone, viz., phenylenephthalide, but it has been shown that when treated with hydroxylamine it yields a body,  $C_{14}H_9O_2N$ , and that lactones are incapable of uniting with hydroxylamine (*Abstr.*, 1883, 1104). It would appear that only one carbonyl-group is acted on in those double ketones in which the two carbonyl-groups are not directly united. H. B.

**Diethyl Alizarin Ether.** By J. HABERMANN (*Monatsh. Chem.*, **5**, 228—231).—Schutzenberger described this body as a bright-yellow substance, insoluble in water, soluble in alcohol; his analytical results are very unsatisfactory.

The author prepares the ether by heating a mixture of alizarin, potassium ethyl sulphate, and potash for some hours at 160—170°. The contents of the tubes are acidulated with sulphuric acid, diluted with water and repeatedly extracted with ether. The ethereal solution is then repeatedly shaken with water rendered slightly alkaline as long as it acquires a violet hue, so as to remove alizarin and any monethyl ether, the ethereal solution is then evaporated and the residue dissolved in chloroform; this solution is then largely diluted with ether, and after being repeatedly shaken with slightly alkaline water, is allowed to evaporate spontaneously. *Diethyl alizarin ether*,  $C_{11}H_6O_2(OEt)_2$ , so obtained, forms aggregates of golden or brownish-yellow needles; it is nearly insoluble in cold, somewhat soluble in hot water, it is more soluble in alcohol and ether, the solutions having a yellow colour. Its best solvent is chloroform. It appears to volatilise unaltered in a current of steam. It dissolves in concentrated nitric acid with golden-yellow colour, but on dilution with water only a few flocks separate. Water added to the dark yellowish-brown solution in concentrated sulphuric acid, precipitates pale-yellow flocks which are not coloured by potash. A. J. G.

**Action of Concentrated Sulphuric Acid on Nitroanthraquinone.** By J. LIFSCHÜTZ (*Ber.*, **17**, 891—899).—This reaction has been studied by several chemists, Liebermann (*Abstr.*, 1883, 597) first showing that the nitro-group suffers reduction whilst some of the hydrogen-atoms are oxidised to hydroxyl-groups. Liebermann's experiments have now been repeated, using a pure nitro-product as starting point, the diorthonitroanthraquinone prepared according to Römer's directions (*Abstr.*, 1883, 737). When this is heated with concentrated sulphuric acid and the product poured into water, it yields

a red-brown precipitate containing four colouring matters, ( $\alpha$ ) red, and ( $\beta$ ) reddish-violet, both soluble in cold alkalis, ( $\gamma$ ) blue and ( $\delta$ ) red, both insoluble in cold alkalis. Cold alcohol dissolves ( $\alpha$ ) not ( $\beta$ ) and ( $\delta$ ) more than ( $\gamma$ ).

$\alpha$  dissolves in alcohol with red, and in alkalis with deep bluish-violet colour; analyses point to the formula  $C_{28}H_{17}N_3O_9$ . A solution of  $\beta$  in benzene or ether or in strong sulphuric acid shows very characteristic and sharp absorption-bands; its alkaline solution is deep blue; its composition is  $C_{28}H_{17}N_3O_{12}$ .  $\gamma$  crystallises from benzene and alcohol in lustrous brown needles; and its solutions also show characteristic absorption-bands, it is  $C_{28}H_{15}N_4O_7$ .  $\delta$  separates from alcohol as a brownish-red crystalline powder; it has the same composition as  $\alpha$ , namely,  $C_{28}H_{17}N_3O_9$ .

Each of these compounds was dissolved in sulphuric acid, and potassium nitrite gradually added, then boiled with absolute alcohol, and precipitated with water; in each case, dihydroxyanthraquinones were obtained.  $\gamma$  yielded anthrarufin, and since it was prepared from diorthonitroanthraquinone, all the hydroxyl- and amido-groups must occupy the  $\alpha$ -position.  $\alpha$  yielded metabenzodihydroxyanthraquinone and a new dihydroxyanthraquinone, insoluble in baryta-water, crystallising from alcohol and ether in deep-red needles melting at  $175-180^\circ$  and volatilising easily; it does not colour mordants; it is probably the last possible and still unknown isomeric dihydroxyanthraquinone. The formula  $C_{28}H_{17}N_3O_9$ , given for  $\alpha$  would, however, yield a dihydroxy- and a trihydroxy-anthraquinone on decomposition; the non-formation of the latter is explained by the reducing action of the nitrous acid. The product  $\beta$  yielded only the last-named dihydroxy-anthraquinone, and here again reduction must have taken place; its formula is  $NH_2.C_{14}HO_2(OH)_4.O.C_{14}H_3O_2(OH)_3.NH_2$ .

$\delta$  gave a substance not completely investigated, but in all probability chrysazin.

H. B.

**Anthraquinonecarboxylic Acid.** C. LIEBERMANN and G. GLOCK (*Ber.*, 17, 888—891).—Liebermann replies to E. v. Meyer's arguments in favour for the new formulæ proposed for anthracene and anthraquinone (*J. pr. Chem.* [2], 29, 138). The unusual stability of the chloride of anthracenecarboxylic acid has been already pointed out (this vol., 329). The chloride and other derivatives of *anthraquinonecarboxylic acid* have been now prepared, to ascertain whether they were also unusually stable. This turns out to be the case, and it is therefore to be remarked that although the corresponding benzene and naphthalene-derivatives behave with reagents like other similar compounds, the anthracene- and anthraquinone-carboxylic acids yield derivatives very much more stable. The compounds examined are:—

*Anthraquinonecarboxylic chloride*, obtained from the carboxylic acid by the action of phosphorous pentachloride. It crystallises well from benzene and melts at  $147^\circ$ . The powdered substance left in contact with 100 times its weight of water for 120 hours was only decomposed to the extent of 7.5 per cent. Benzoic chloride is completely decomposed in six hours, and the chlorides of  $\alpha$ - and  $\beta$ -naphthoic acids are very easily decomposed.

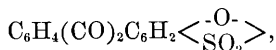
*Ethyl anthraquinonecarboxylate*, obtained by decomposing the chloride with alcohol; 18 hours are requisite when cold. It is easily soluble in alcohol, from which it separates in crystals melting at 147°.

*Anthraquinonecarborylamide* is formed by the action of ammonia gas on a solution of the chloride in benzene. It is also remarkably stable; it is not acted on when boiled with weak potash solution, and it is also unaffected by strong sulphuric acid.

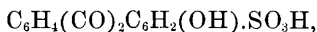
*Anthraquinonecarboxylanilide* is formed comparatively easily by the action of aniline on the chloride.

Anthraquinonecarboxylic acid also yields substitution-products with difficulty, the action of bromine is very slight at over 200°; strong nitric acid has no effect, but in presence of strong sulphuric acid there is formed *mononitroanthraquinonecarboxylic acid*. H. B.

**Action of Concentrated Sulphuric Acid on  $\alpha$ -Nitro-anthraquinonesulphonic Acid, and the Constitution of the Latter.** J. LIFSCHÜTZ (*Ber.*, 17, 899—902).— $\alpha$ -Nitroanthraquinonesulphonic acid was prepared from sodium meta-anthraquinonesulphonate by Claus' method (*Abstr.*, 1882, 1105). The position of the nitro-group was determined by converting the body into the corresponding dihydroxyanthraquinone as follows: the amido-acid, prepared by reduction of the nitro-derivative with tin and hydrochloric acid, was dissolved in boiling acetic acid and treated with dilute solution of potassium nitrite, when *erythrohydroxyanthraquinonesulphonic anhydride*,



is deposited in grey needles; it decomposes below 100°, is a very insoluble body; cold caustic soda solution does not dissolve it, but when hot it does; from this solution concentrated hydrochloric acid precipitates *erythrohydroxyanthraquinonesulphonic acid*,



as a yellow powder. The free acid is easily soluble and yields soluble salts, their solutions being red; the silver salt crystallises in golden needles. When the free acid or the anhydride is fused with alkalis, it easily yields alizarin; it is not identical with any of the four acids so far known.

When nitro-anthraquinonesulphonic acid is heated with concentrated sulphuric acid at 211° and the product treated with water, it yields a red compound which crystallises from its alcoholic solution on addition of ether; it is a *dihydroxyamidoanthraquinonesulphonic acid*,  $\text{C}_{14}\text{H}_4\text{O}_2(\text{OH})_2(\text{NH}_2)\cdot\text{SO}_3\text{H}$ . As this is the formula originally given by Liebermann (*Abstr.*, 1883, 597), it is in favour of the arguments against the formulæ proposed by Claus. H. B.

**Phthalacene-derivatives.** By S. GABRIEL (*Ber.*, 17, 1397—1400).—*Phthalacene oxide*,  $\text{C}_{21}\text{H}_{14}\text{O}$ , is obtained by oxidation of phthalacene (p. 1176) with chromic acid; it forms compact citron-yellow crystals, and melts at 211—214°.

*Bromphthalacene*,  $\text{C}_{21}\text{H}_{13}\text{Br}$ , is obtained by the action of bromine on

a solution of phthalacene in hot glacial acetic acid: it forms colourless lustrous crystals, melts at  $184-184.5^{\circ}$ , and is less soluble than phthalacene in boiling acetic acid. On oxidation, it is converted into *bromophthalacene oxide*,  $C_{21}H_{13}BrO$ , crystallising in glittering, flat, yellow needles, which melt at  $200^{\circ}$ .

*Dinitrophthalacene*,  $C_{21}H_{14}(NO_2)_2$ , obtained by nitration of phthalacene in the cold with a mixture of acetic and nitric acids, crystallises in small brownish-yellow needles, sinters together at  $270-280^{\circ}$ , and is completely decomposed on further heating.

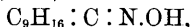
*Oximidophthalacene*,  $C_{21}H_{14}:NOH$ , is obtained by heating a mixture of hydroxylamine hydrochloride and phthalacene oxide with alcohol and a few drops of hydrochloric acid for two hours at  $150-160^{\circ}$ . It crystallises in lustrous yellow needles, and melts at  $265-266^{\circ}$ . The formation of this substance shows that phthalacene oxide contains a CO-group.

By heating phthalacene oxide with finely powdered soda lime for 6 to 7 hours at  $350^{\circ}$ , there is obtained, in small quantity, the calcium salt of a new acid. *Phthalacenic acid*,  $C_{20}H_{15}.COOH$ , forms pale yellow compact crystals, and melts at  $245-247^{\circ}$ . A. J. G.

**Synthesis of a Terpene.** By R. RADZISZEWSKI and J. SCHRAMM (*Ber.*, 17, 838-840).—Amylene from fusel oil, boiling at  $35-37^{\circ}$  (mostly trimethylethylene), was converted into the hydrochloride, and this was heated with dilute ammonia at  $110-120^{\circ}$ . On adding potash to the product and purifying the oily layer which separated, two bases were isolated, namely, *oxyisoamylamine*,  $C_5H_{11}O.NH_2$ , and *dioxyisoamylamine*,  $(C_5H_{11}O)_2NH$ ; the base  $C_5H_9.NH_2$ , observed by Wurtz, was not formed. The first base boils at  $157-159^{\circ}$ , and has a strongly alkaline reaction; its platinochloride is easily soluble in water. The second base is viscous, and boils at  $249-251^{\circ}$ ; its platinochloride and aurochloride are very soluble and not crystallisable.

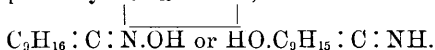
The action of phosphorous pentoxide on oxyisoamylamine is very energetic; the bulk of the product consists of a liquid smelling of turpentine oil, and distilling at  $155-156^{\circ}$ . The composition of the oil is very nearly expressed by  $C_{10}H_{16}$ , and it absorbs oxygen from the air and becomes very viscous. H. B.

**Camphoroxime.** By E. NÄGELI (*Ber.*, 17, 805-807).—In previous papers (*Abstr.*, 1883, 728, and this vol., 610) camphoroxime,



and the so-called anhydride,  $C_9H_{15}:C:N$ , have been described. By

heating the anhydride with alcoholic potash, there are obtained an oil, not fully examined, and a white crystalline substance of the same composition as camphoroxime, but it melts at  $125^{\circ}$  (camphoroxime at  $115^{\circ}$ ), and does not yield an ether when treated with sodium methylate and methyl iodide, moreover it is quite odourless; the body may therefore be called *isocamphoroxime*. Since the anhydride does not yield an acid on saponification, it cannot be a nitrile,  $C_9H_{15}.CN$ , but is probably  $C_9H_{15}:C:N$ ; in this case isocamphoroxime will be either



H. B.

**The Quinovin Group.** By C. LIEBERMANN (*Ber.*, **17**, 868—875).—The previous work of Liebermann and Giesel (*Ber.*, **16**, 926) has been confirmed by Oudemans; the following are further observations. Quinovic acid, like pyroquinovic acid, gives a red coloration with strong sulphuric acid. *Ethyl quinovate*,  $C_{32}H_{46}EtO_6$ , when freshly prepared from potassium quinovate and ethyl iodide, is an oil which crystallises after very long standing; it melts at 127—130°. Pyroquinovic acid, when crystallised from glacial acetic acid, seems to combine with it, for the acid is only removed by long heating at 130°. Novic acid and its salts have almost the same composition as those of pyroquinovic acid, but the alkaline solution of the latter acid is lævoro-rotatory acid, and that of novic acid strongly dextrorotatory. Novic, quinovic, and pyroquinovic acids when distilled yield a resinous distillate; this contains oxygen compounds which may be removed by heating with strong hydriodic acid and phosphorus. On redistillation, *quinoterpene*,  $(C_{10}H_{16})_3$ , a dextrorotatory terpene, is obtained; it can also be prepared by treating pyroquinovic acid with hydriodic acid and phosphorus. The resinous body obtained during the preparation of quinochromin is essentially the same substance. Assuming quinoterpene to be  $C_{30}H_{48}$ , from its high boiling point, quinovic acid is  $C_{30}H_{46}O_2(COOH)_2$  and pyroquinovic acid  $C_{30}H_{47}O_2.COOH$ , whilst quinochromin is  $C_{30}H_{46}O_2$ . Giesel has obtained from quinovaresin a crystalline indifferent substance,  $C_{30}H_{46}O_2$ ; it melts at 139°, and distils at over 360°; with hydriodic acid, it yields a viscous mass,  $C_{10}H_{16}$ , hence the name *oxyquinoterpene* is proposed for this body. When quinochromin is treated with reducing agents, coloured products are obtained, but they are not identical with oxyquinoterpene. In small quantities, quinovite,  $C_6H_{12}O_4$ , may be distilled without decomposition at 297—305°. *Acetylquinovite*,  $C_6H_9O(OAc)_3$ , forms white needles melting at 46—47°, and boiling at about 303°; when heated with dilute acids, it is resolved into quinovite and acetic acid. Quinovite has the same composition as a body prepared by Bourchardt from dulcite and the mannide prepared by Berthelot from mannite. The author failed to prepare an acetyl-derivative of mannide, which also differs from quinovite in not reducing Fehling's solution. The quantity of quinovin occurring in the various barks is very different; from 7 to 16 grams pure quinovin being obtainable from 12 kilos. of the bark.

H. B.

**Viola-quercitrin, a new Glucoside.** By K. MANDELIN (*Bied. Centr.*, 1884, 285).—Viola-quercitrin,  $C_{42}H_{72}O_{21}$ , obtained from *Viola tricolor*, var. *arvensis*, is yellow, soluble in alkalis and boiling water and is crystalline. When treated with acids, it is decomposed into 3 mols. of a fermentable sugar and 1 mol. quercetin, which is identical with that obtained from quercitrin.

E. W. P.

**Asarone and the Ethereal Oil of Asarum Europæum, L.** By T. POLECK (*Ber.*, **17**, 1415—1416).—The paper by Rizza and Butlerow on asarone (this vol., 1042) has caused the author to publish the results he has obtained along with Staats on this subject, although their investigations are still far from complete. Pure

asarone is markedly phosphorescent, melts at  $61^{\circ}$ , can be distilled in small quantities, is readily soluble in light petroleum, alcohol, ether, and chloroform, slightly soluble in boiling water. It is without odour. By reduction with zinc-dust, it yields a small quantity of a liquid product and a not inconsiderable amount of a mixture of gases, containing CO about 30 per cent.,  $\text{CH}_4$  36 per cent.,  $\text{H}_2$  26 per cent., hydrocarbons absorbed by sulphuric acid 2 per cent.,  $\text{CO}_2$  none. By oxidation, best with potassium permanganate, there were obtained carbonic anhydride, formic, acetic, and oxalic acids, a solid acid crystallising from ether in needles, and melting at  $144^{\circ}$ , and a substance of neutral reaction crystallising in slender silky needles melting at  $117^{\circ}$ , and soluble in water. Analysis led to the empirical formula  $\text{C}_8\text{H}_8\text{O}_3$ . The authors continue their work on this subject.

A. J. G.

**Quassin and its Constitution.** By V. OLIVERI and A. DENARO (*Gazzetta*, 14, 1—9).—In order to prepare quassin from quassia, 10 kilos. of the finely divided wood are twice extracted with 45 litres of boiling water, and the solution evaporated to 10 litres *at a gentle heat*; when cold, the quassin is precipitated by tannin, collected, washed, and after being mixed with a sufficient quantity of lead carbonate, it is thoroughly dried at  $100^{\circ}$ . The product is then extracted with boiling alcohol, the alcohol distilled off, and the residue set aside until it deposits the quassin in a crystalline state: it is, however, always contaminated with resinous matters, from which it is purified by repeated crystallisations from dilute alcohol: 30 kilos. of the wood gave 10 grams of pure quassin. It crystallises in very slender, colourless, iridescent needles, which belong to the monoclinic system, the predominating form being the oblique prism with rhombic base. It melts at  $210\text{--}211^{\circ}$  (Christensen  $205^{\circ}$ ), and is very soluble in alcohol, chloroform, and acetic acid, but only sparingly in ether: 100 parts of water at  $22^{\circ}$  dissolve 0.2529; the aqueous solution becomes yellow on exposure to the air, is dextrorotatory, excessively bitter, and reduces Fehling's solution. The results of the analyses agree nearly with the numbers required by the formula  $\text{C}_{32}\text{H}_{44}\text{O}_{10}$ , and differ considerably from those given by Wiggers and by Christensen, who proposed the formulæ  $\text{C}_{10}\text{H}_{12}\text{O}_5$  and  $\text{C}_{31}\text{H}_{42}\text{O}_9$  respectively.

When quassin is heated at  $90^{\circ}$  for some hours with dilute sulphuric acid (4 per cent.), it yields *quasside*,  $\text{C}_{32}\text{H}_{42}\text{O}_9$ , a white, amorphous, bitter substance, formed from quassia by the removal of the elements of 1 mol.  $\text{H}_2\text{O}$ ; no glucose could be detected in the mother-liquors. It melts at  $192\text{--}194^{\circ}$ , and when boiled with dilute alcohol is reconverted into quassin, which crystallises out as the solution cools. Quasside is also formed when quassin is boiled with acetic anhydride, but if sodium acetate is present there is a powerful reaction, and several substances seem to be produced; these have not as yet been submitted to examination.

Bromine diluted with acetic acid acts on a solution of quassin in the same solvent, and on adding water an amorphous resinous substance is obtained, but it does not crystallise; this melts with decomposition at  $155^{\circ}$ , and the results of the analyses suggest the formula  $\text{C}_{32}\text{H}_{41}\text{Br}_3\text{O}_9$ . Nitric acid added to an acetic solution of quassin seems

to give rise to a nitro-derivative, which is precipitated on the addition of water. It dissolves in boiling alcohol, and, as the solution cools, is deposited again as a yellowish powder which melts at  $130^{\circ}$ .

If quassin is heated with concentrated hydrochloric acid in sealed tubes for four hours at  $100^{\circ}$ , methyl chloride is formed and escapes on opening the tubes; whilst the hydrochloric solution, when diluted with water, deposits first a resinous matter, which should be removed, and then, after a time, a colourless substance in small nodules. This new compound, which the author calls *quassic acid*,  $C_{14}H_{19}O_3 \cdot COOH$ , or  $C_{28}H_{38}O_6(COOH)_2$ , is far less soluble in alcohol than quassin, and crystallises in silky needles which melt at  $245^{\circ}$ , and reduce Fehling's solution and ammoniacal silver nitrate in the cold. It seems to be formed thus:  $C_{32}H_{44}O_{10} + 2HCl = C_{28}H_{38}O_6(COOH)_2 + 2CH_3Cl$ , so that quassin would be the ethereal salt of quassic acid. The author has also tried the action of nascent hydrogen, and of boiling dilute nitric acid on quassin, but the products are resinous. Fusion with potash and oxidation with chromic anhydride also gave unsatisfactory results.

The resinous matter obtained in the preparation of crystallised quassin, and in all probability produced from the latter, was submitted to distillation with zinc-dust. The brown oily product was treated with sodium and fractionally distilled; the portion passing over at  $170$ — $190^{\circ}$  when again distilled gave an oil boiling at  $173$ — $178^{\circ}$  of the formula  $C_{11}H_{16}$ , whilst crystals melting at  $76$ — $78^{\circ}$  were obtained from the residue in the retort.

C. E. G.

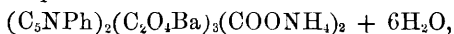
**New Methods for the Formation of  $\alpha$ -Carbopyrrolic Acid from Pyrroline.** By G. CIAMICIAN and P. SILBER (*Ber.*, **17**, 1437—1439).— $\alpha$ -Carbopyrrolic acid can be prepared from pyrroline by heating it with carbon tetrachloride and alcoholic potash. It is also formed, together with another acid, by the action of carbonic anhydride on the fused potassium-derivative of pyrroline. Attempts to prepare the aldehyde of carbopyrrolic acid by the action of chloroform on pyrroline in presence of potash were unsuccessful, nothing but resinous products being obtained.

A. J. G.

**Constitution of Pyridine.** By A. HANTZSCH (*Ber.*, **17**, 1512—1522).—With the hope of throwing light on the constitution of the pyridine nucleus, the author has investigated the constitution of the pyridine-derivatives obtained by the condensation of ammonio-aldehydes with ethyl acetoacetate. Ethyl phenyl-lutidinedicarboxylate,  $C_8NPhMe_2(COOEt)_2$ , already described by Schiff and Puliti (*Abstr.*, 1883, 1151) was saponified with alcoholic potash. The neutral potassium salt, which is easily soluble in alcohol, was then oxidised by means of potassium permanganate. The oxidation takes place more regularly than with ethyl collidinedicarboxylate. The solution is filtered from precipitated manganic oxide and treated with excess of concentrated nitric acid, when *trihydrogen potassium phenylpyridine-tetracarboxylate*,  $C_{15}H_8NO_8K + H_2O$ , crystallises out in small prisms or pyramids, sparingly soluble in cold water, and having a strongly acid reaction and taste. *Paraphenylpyridinetetracarboxylic acid*,



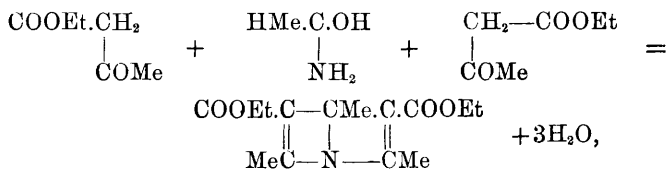
$C_5NPh(COOH)_3$ , forms small glittering crystals containing  $3H_2O$ , which it loses at  $120^\circ$ . It melts at  $205-207^\circ$  with evolution of carbonic anhydride. It is easily soluble in water, rather sparingly in ether. It is best obtained pure from the trihydrogen potassium salt; this salt is covered with a little water, excess of concentrated sulphuric acid added, and the whole warmed until the crystals of the salt are completely dissolved: as the solution cools, the acid crystallises out in a pure state. Its neutral ammonium salt is precipitated by *mercurous, lead, and silver salts*: on heating with ferric chloride a flocculent precipitate, and with cadmium sulphate a crystalline precipitate is produced. The *copper salt*,  $C_5NPh(COO)_2Cu + 7H_2O$ , crystallises in small blue rhombohedrons, which when once formed are quite insoluble in water. Barium chloride, even in presence of excess of ammonia, precipitates a double salt of the formula



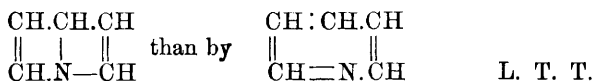
in the form of microscopic plates. It loses its water of crystallisation at  $130^\circ$ .

*Paraphenylpyridine*,  $C_5NPhH_4$ , is obtained by the dry distillation of trihydrogen potassium phenylpyridinetetracarboxylate, but the yield is much better if the salt is first intimately mixed with its own weight of lime. It distils at  $274-275^\circ$  (uncorr.), and solidifies to a glistening white mass which melts at  $77-78^\circ$ . It is thus different from the  $\alpha$ - and  $\beta$ -phenylpyridines described by Skraup (*Wiener Monatsh.*, 1884, 436), which are liquid and both boil at  $269-270^\circ$ . It has the odour of diphenylamine, and volatilises slowly in a current of steam. It dissolves in warm hydrochloric acid, and yields a *hydrochloride* crystallising in needles. The *platinochloride*,  $(C_5NPhH_4)_2H_2PtCl_6$ , is anhydrous, and crystallises in microscopic nodules. The *picrate* crystallises in yellow needles, which soften at  $190^\circ$  and melt at  $195-196^\circ$ . The *dichromate*,  $(C_5NPhH_4)_2H_2Cr_2O_7$ , crystallises in long orange-coloured needles which melt at  $155^\circ$  with partial decomposition.

When oxidised with potassium permanganate,  $\gamma$ -phenylpyridine yields isonicotinic (or  $\gamma$ -pyridinecarboxylic) acid. This acid has been proved by Skraup to be the para-acid, so that the phenyl-group, in all the above-mentioned substances, must be in the para-position to the N-atom. It is thus clear that in the formation of ethyl phenyl-lutidinedicarboxylate the phenyl of the ammoniobenzaldehyde takes the para-position to the N-atom, and it is therefore probable that in the formation of ethyl collidinedicarboxylate the methyl of the ammonioaldehyde takes the same position. The author thinks that the formation of the latter body would be as follows:—



and that the constitution of pyridine would be more correctly explained by the formula



**Pyridine-derivatives.** By W. KÖNIGS and R. GEIGY (*Ber.*, **17**, 589—595).—Königs and Körner (this vol., 85) have shown that when quinolinic acid is fused with potash it forms a hydroxyquinolinic acid, which differs from Lieben and Haitinger's ammonio-chelidonic acid (*Abstr.*, 1883, 871), inasmuch as when heated with water at 195° it is resolved into carbonic anhydride and a *hydroxypyridinemonocarboxylic acid*,  $\text{C}_6\text{H}_5\text{NO}_3$ ; this acid crystallises from hot water in colourless crystals melting at 301—302°; with ferric chloride it yields a yellow coloration. The solutions of its sodium salt give immediate precipitates with copper, lead, and silver salts, and with barium and calcium salts after boiling. The lead salt,  $(\text{C}_6\text{H}_4\text{NO}_3)_2\text{Pb} + \frac{1}{2}\text{H}_2\text{O}$ , crystallises from hot water in white needles.

The formation of hydroxypyridine by the distillation of hydrogen silver hydroxyquinolate, observed by Königs and Körner, has been confirmed by the authors, who have subjected this compound to further investigation. Its aqueous solution gives a red coloration with ferric chloride, and with silver nitrate and ammonia a precipitate soluble in excess of ammonia. Its hydrochloride separates in white needles when hydrochloric acid gas is passed into an ethereal solution of hydroxypyridine. Its aqueous solution, treated with bromine-water, yields a *dibromohydroxypyridine*,  $\text{C}_5\text{H}_2\text{Br}_2\text{NO}$ , which crystallises from water in white needles melting at 206—207°. It is different from the dibromohydroxypyridine described by Hofmann (*Abstr.*, 1879, 733), also from that obtained by Lieben and Haitinger (*loc. cit.*), and that prepared by Ost from comenamic acid (*J. pr. Chem.* [2], **29**, 65). The formation of this hydroxypyridine is similar to the production of carbostyryl, and it therefore probably has the constitution  $[\text{N} : \text{OH} = 1 : 2]$ .

*Pyridinedisulphonic Acid.*—The production of this acid by the treatment of piperidine with concentrated sulphuric acid has already been described by Königs and Hofmann (*Abstr.*, 1883, 1143). It is very soluble in water, but almost insoluble in ether, alcohol, and glacial acetic acid; it crystallises from water in white needles. The potassium, lead, and sodium salts are all well-defined crystalline compounds, the latter containing 4 mols. of  $\text{H}_2\text{O}$ , and the lead salt  $4\frac{1}{2}$  mols. The disulphonic acid, when treated with bromine, is converted into a *dibromopyridine* melting at 164°. *Barium pyridinedisulphonate* is scarcely acted on by phosphorous pentachloride at 130—150°, but at 200° a reaction takes place with formation of a mixture of a *dichloro-* and *trichloro-pyridine*, from which, by repeated crystallisations from alcohol, the latter compound may be obtained in lustrous plates melting at 48°. P. P. B.

**Synthesis of Pyridine and Piperidine Bases.** By A. LADENBURG (*Ber.*, **17**, 772—774).—The action of heat on pyridine ethiodide has been already noticed (*Ber.*, **16**, 2059), the action on pyridine propiodide is now described. Pyridine and propyl iodide are heated

at 290°, and the product distilled with potash, by which means it is separated into three portions, namely, pyridine, a portion boiling at 160—164°, and a third fraction boiling at 173—175°.

The second portion is *propylpyridine*,  $C_8H_{11}N$ , as is shown by its analysis and vapour-density; it boils at 162°, and its sp. gr. at 0° is 0.9393. The aurochloride and platinochloride,  $(C_8H_{11}N)_2H_2PtCl_6$ , are moderately soluble. Potassium permanganate converts it into  $\gamma$ -pyridinecarboxylic acid, melting at 305°; the base is therefore  $\gamma$ -propylpyridine.

The third portion resembles greatly in odour and specific gravity, &c., the second portion, but the aurochloride and platinochloride are more sparingly soluble; it is also a propylpyridine, but whether of the  $\alpha$  or  $\beta$  series, cannot be decided, an acid being obtained on oxidation which does not appear to be a pyridinecarboxylic acid at all.

If these two propylpyridines are treated with sodium and alcohol, they yield propylpiperidines,  $C_8H_{17}N$ . The  $\gamma$ -compound boils at 157—161°, and its sp. gr. at 0° is 0.870; its aqueous solution is rendered turbid by heat, but not very readily. The other base boils at 165—168°, and also smells very much like conine, the aqueous solution is at once rendered turbid on warming, but it is optically inactive. It has many properties in common with conine, and like it is poisonous, acting in the same manner and to the same degree; the  $\gamma$ -base and its salts are not so active. It is possible that the higher boiling base contains some  $\alpha$ -propylpiperidine (*i.e.*, conine), although in two optical modifications. The researches are being continued.

H. B.

**Nitrogenous Derivatives of Chelidonic Acid.** By A. LIEBEN and L. HATTINGER (*Ber.*, **17**, 1507—1508).—Ost has found (*J. pr. Chem.*, [2], **29**, 57 and 378) that his hypothetical pyridine is the hydroxypyridine obtained by the authors from chelidonic and ammonio-chelidonic acids. The authors have now obtained a *hydroxymethylpyridine*,  $C_6H_7ON$ , in the following ways:—1, action of methyl iodide and potash on hydroxypyridine; 2, action of methyl iodide on hydroxypyridine, and treatment of the product with silver oxide; and 3, by heating methylammoniochelidonic acid. This body is a crystalline but very deliquescent substance, which yields a crystalline platinochloride. With bromine, it yields the same dibromo-derivative,  $C_6H_5Br_2ON$ , melting at 192°, as is obtained by the action of methyl iodide and potash on hydroxydibromopyridine. *Methylammoniochelidonic acid* is a crystalline substance prepared by the action of methylamine on chelidonic acid. Aniline, in like manner, yields *phenylammoniochelidonic acid*. Dimethylamine, like the mineral alkalis, decomposes chelidonic acid into oxalic acid and acetone. It seems to act like a primary amine with phenylhydrazine.

L. T. T.

**Metachloroquinoline.** By W. LA COSTE and J. BODEWIG (*Ber.*, **17**, 926—928).—The parachloroquinoline has been previously described (*Abstr.*, 1882, 979). Metachloroquinoline was prepared by Skraup's reaction, using metachloraniline and nitrobenzene. By mixing a solution of the sulphate with a sufficient quantity of potassium dichromate, and allowing it to stand, crystals of *metachloroquinoline*

*chromate*,  $(C_9H_6ClN)_2 \cdot H_2Cr_2O_7$ , separate. The crystals require more than 400 parts of cold water for solution. *Metachloroquinoline* is an oil boiling at  $264-266^\circ$ , and scarcely soluble in water. The hydrochloride,  $C_9H_6ClN \cdot HCl$ , is deliquescent; the platinochloride,  $(C_9H_6ClN)_2 \cdot H_2PtCl_6 + 2H_2O$ , is a brownish-yellow precipitate, which may be crystallised from dilute hydrochloric acid. Metachloroquinoline unites with methyl iodide to form metachloroquinoline methiodide,  $C_9H_6ClN \cdot MeI$ , in yellow needles melting at  $231-232^\circ$ , and having an intensely bitter taste. When metachloroquinoline is heated with nitric and sulphuric acids, it yields two isomeric nitro-derivatives.  *$\alpha$ -Nitrometaquinoline* melts at  $185-186^\circ$ , and crystallises from the alcoholic solution first, it is sparingly soluble even in warm alcohol.  *$\beta$ -Nitrometachloroquinoline* melts at  $129-123^\circ$ , and is easily soluble in hot alcohol. Both compounds yield crystalline platinochlorides, and by tin and hydrochloric acid they are reduced to amido-derivatives. H. B.

**Dimethylquinoline.** By L. BEREND (*Ber.*, 17, 1489-1490).—This was prepared by Skraup's reaction from orthoxylidine, nitrobenzene, glycerol, and concentrated sulphuric acid. *Dimethylquinoline*,  $C_{11}H_{11}N$ , is a yellowish liquid boiling at  $273-274^\circ$ . Its platinochloride,  $(C_{11}H_{11}N)_2 \cdot H_2PtCl_6 + H_2O$ , crystallises in pale yellow microscopic needles. The acid sulphate crystallises in prisms which effloresce on exposure to the air, and appear to contain water of crystallisation. The chromate yields small orange needles, sparingly soluble in boiling water. Fuming sulphuric acid at  $115-120^\circ$  yields a crystalline sulphonic acid which melts at  $265-266^\circ$ . This acid, on fusion with potash, gives a dimethylquinophenol, which is volatile in steam, and yields a platinochloride, crystallising in pale yellow needles. As the amido-group is in the para-position in orthoxylidine, the two methyl groups in dimethylquinoline must be contiguous.

L. T. T.

**Some Derivatives of Quinolinemetacarboxylic Acid.** By O. FISCHER and G. KÖRNER (*Ber.*, 17, 765-766).—In a previous paper, (*Abstr.*, 1882, 412 and 869) the preparation of the ortho- and metacyanoquinolines is described, and also (*Abstr.*, 1882, 71) the quinolinecarboxylic acids. During the preparation of orthocyanquinoline, a large quantity of the meta-compound is always formed.

*Tetrahydroquinolinemetacarboxylic acid*,  $C_{10}H_{11}NO_2$ , is prepared by treating the quinolinemetacarboxylic acid with zinc and hydrochloric acid at  $100^\circ$ ; a portion of the product separates as zinc salt, the rest is extracted with ether. It crystallises from alcohol in long colourless needles or plates, which melt at  $146-147^\circ$ . Treated with a nitrite in acid solution, it yields a nitroso-body,  $C_{10}H_{10}N_2O_3$ , crystallising in fine yellow prisms from alcohol.

*Kairolinmetacarboxylic acid*,  $C_{10}H_{10}MeNO_2$ .—The preceding acid is heated with the necessary amount of ethyl iodide at  $140-150^\circ$ ; the product is dissolved in water, and the solution mixed with sodium acetate, when the new acid separates out; it crystallises from alcohol in needles which melt at  $164^\circ$ ; on allowing the mother-liquor to remain for a time, the methyl iodide additive-compound separates in

large crystals. This acid receives the above name, as König and Hoffmann have given the name kairolin to tetrahydromethylquinoline.

H. B.

**Synthesis of Quinoline-derivatives.** By L. KNORR (*Ber.*, **17**, 540—546).—The continuation of the investigation of the method of preparing quinoline-derivatives by the action of primary amines on ethyl acetoacetate has yielded the following results:—

*Phenyl-β-imidobutyric acid*,  $\text{PhN} : \text{CMe} \cdot \text{CH}_2 \cdot \text{COOH}$ , is formed when aniline and ethyl acetoacetate are heated in sealed tubes at 150—160°, it is soluble in water, ether, &c., and has both acid and basic properties. Ferric chloride imparts to its solutions a dark violet coloration, destroyed by hydrochloric acid. Sulphuric acid in the cold, and hydrochloric acid after continued heating, convert it into *γ-hydroxyquinaldine*, an oily liquid.

*Orthotolyl-β-imidobutyric acid* is obtained from orthotoluidine and ethyl acetoacetate, it crystallises in flat needles, and by concentrated sulphuric acid is converted into *orthotoluene-γ-hydroxyquinaldine*,  $\text{C}_{11}\text{H}_{11}\text{ON}$ , a solid melting at 185°.

*Paratolyl-β-imidobutyric acid*,  $\text{C}_{11}\text{H}_{13}\text{NO}_2$ , is obtained from paratoluidine; sulphuric acid converts it into the corresponding *γ-hydroxyquinaldine*, melting at 245°.

*β-Naphthyl-β-amidobutyric acid*,  $\text{C}_{14}\text{H}_{13}\text{NO}_2$ , is formed by the action of *β*-naphthylamine on ethyl acetoacetate, it crystallises from water in needles which melt at 92°. At the same time, a considerable quantity of the naphthalide of this acid is formed, a compound crystallising from benzene in needles melting at 200°; this, when heated with hydrochloric acid, yields a further quantity of *β*-naphthyl-β-imidobutyric acid. When the acid is heated with concentrated hydrochloric acid it yields *β-naphtha-γ-hydroxyquinaldine*, which crystallises from alcohol in flat shining needles, melting at 286°. It exhibits marked resemblance to *γ-hydroxyquinaldine*, and is volatile without decomposition. Distilled with zinc-dust, it yields a volatile base melting at 91—92°, having all the properties of naphthoquinaldine; its solutions in strong acids have a green fluorescence and an intense blue in dilute acids. Its *platinochloride*,  $(\text{C}_{11}\text{H}_{11}\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$ , is sparingly soluble in hot dilute hydrochloric acid. This base differs from the quinaldine prepared by Döbner and Miller's method.

*α-Naphthylamine* yields condensation-products with ethyl acetoacetate, the *α*-naphtho-*γ*-hydroxyquinaldine melts at 292°.

*Phenylenedi-imidobutyric acid*,  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_4$ , is obtained by heating orthophenylenediamine with ethyl acetoacetate at 170°; it crystallises in plates which melt at 176°.

Ethyl succinosuccinate behaves with the aromatic primary amines as ethyl acetoacetate does; when heated with paratoluidine at 200° it yields a compound,  $\text{C}_{31}\text{H}_{33}\text{N}_3\text{O}_3$ , crystallising from alcohol in needles which melt at 263°. It is insoluble in ordinary solvents, acids, and alkalis. Aniline yields a similar compound, melting at 210°.

P. P. B.

**Derivatives of Toluquinoline.** By J. HERZFELD (*Ber.*, **17**, 903—906; comp. this vol., 1051, and next Abstract).—*α-Methyl-γ-quinolinemonosulphonic acid*,  $[\text{N} : \text{CH}_3 : \text{SO}_3\text{H}, 1' : 1 : 3]$ , orthamidometa-

toluenesulphonic acid, prepared from orthotoluidine, was heated with nitrobenzene, glycerol, and sulphuric acid, and the product poured into water. It forms colourless prisms, only slightly soluble in water. *γ-Hydroxy-α-methyl-quinoline* is formed by fusing the above with caustic soda. It is not volatile with steam, crystallises from ether, and melts at 200°.

*α-Methyl-δ-quinolinemonosulphonic Acid*.—Orthonitrotolueneparasulphonic acid is reduced by sulphuretted hydrogen, and the amido-acid converted into the substituted quinoline by Skraup's method as before. It crystallises well from water. *Hydroxy-α-methylquinoline* is obtained from the preceding by fusion with potash; it melts above 260°.

The author has endeavoured to obtain the same bodies directly from toluquinoline. Orthotoluquinoline, boiling at 246–248°, was heated at 135–140° with fuming sulphuric acid, and precipitated with water; two acids are formed, one sparingly soluble in water, the other easily soluble. The first, *orthotoluquinoline-(a)-monosulphonic acid*, yields a sparingly soluble barium salt; fused with alkalis it yields *(a)-hydroxyorthotoluquinoline*, melting at 94–96°, and volatile with steam. The second, *orthotoluquinoline-(b)-monosulphonic acid*, forms an easily soluble barium salt. The corresponding *(b)-hydroxy-orthotoluquinoline* is not volatile with steam; it melts at 92–93°.

H. B.

**Derivatives of Toluquinoline.** By J. HERZFELD (*Ber.*, 17, 1550–1553).—The author previously described two toluquinoline-sulphonic acids, *a* and *b* (preceding Abstract), which he had prepared from a commercial sample of toluquinoline of constant boiling point, 246–248°, and which he believed to be the ortho-compound. He has now for comparison prepared the sulphonic acids from pure bodies.

*Orthotoluquinolinemonosulphonic acid* was obtained by the action of fuming sulphuric acid (sp. gr. 1.89) on pure orthotoluquinoline, boiling at 248°. It crystallises in brilliant colourless prismatic needles. The acid and its barium and potassium salts are easily soluble in water. The barium salt forms anhydrous rhombic needles; the potassium salt, large plates. *Orthohydroxyquinoline*, obtained by fusing the sulphonic acid with sodium hydroxide, melts at 245–248° with partial decomposition. It is not volatile in steam, but may be sublimed with care, and yields tufts of needles. It gives a reddish-brown coloration with ferric chloride. It dissolves in soda and potash, and an alcoholic solution of these compounds, when digested with methyl iodide, yields *orthomethoxytoluquinoline*. This is a dark-red oil, boiling at 225–230°. Its platinumchloride crystallises in yellow needles. The above sulphonic acid and other derivatives are therefore identical with the *b* acid and its derivatives before described.

*Paratoluquinolinemonosulphonic acid*, prepared from pure paratoluquinoline boiling at 259–261° (corr.), crystallises in scales. Its alkali salts are easily soluble; the barium, calcium, and copper salts sparingly so. *Parahydroxytoluquinoline* is volatile in steam, crystallises in colourless needles, and melts at 95–96°. Its platinumchloride forms orange needles. *Paramethoxytoluquinoline* is a yellowish-brown oily mass, which may be distilled. The crystalline platinumchloride is brown. The parasulphonic acid and its derivatives are therefore

identical with the  $\alpha$  acid and derivatives previously described. It is thus clear that the commercial toluquinoline used in the previous experiments must have been a mixture of the ortho- and para-compounds, notwithstanding that it boiled constantly within less than two degrees of the boiling point of orthotoluquinoline. L. T. T.

**Quinaldinecarboxylic Acids.** By O. DOEBNER and W. v. MILLER (*Ber.*, **17**, 938—944).—The action of the three amidobenzoic acids on aldehyde, in presence of hydrochloric acid, has been examined to ascertain whether the carboxyl-group had any modifying action. The reaction, however, proceeds quite normally (this vol., p. 183), quinaldinecarboxylic acid,  $\text{COOH.C}_6\text{H}_3\langle\begin{smallmatrix} \text{N:CMe-} \\ \text{CH:CH} \end{smallmatrix}\rangle$ , being formed.

*Paraquinaldinecarboxylic Acid.*—The reagents, hydrochloride of paramidobenzoic acid, paraldehyde, and hydrochloric acid, react with development of heat, and the hydrochloride of paraquinaldinecarboxylic acid separates out; it is purified by recrystallisation from dilute hydrochloric acid. On adding the requisite quantity of sodium carbonate to a solution of the hydrochloride, the free acid is deposited as a sandy powder, only slightly soluble even in hot water. It forms salts with both acids and bases. The hydrochloride,  $\text{C}_{11}\text{H}_9\text{NO}_2\cdot\text{HCl} + \text{H}_2\text{O}$ , is soluble in water, but not in dilute acid; the platinochloride,  $(\text{C}_{11}\text{H}_9\text{NO}_2)_2\cdot\text{H}_2\text{PtCl}_6 + 4\text{H}_2\text{O}$ , is only slightly soluble; the chromate,  $(\text{C}_{11}\text{H}_9\text{NO}_2)_2\cdot\text{H}_2\text{Cr}_2\text{O}_7$ , is also only slightly soluble in cold water. The calcium salt,  $(\text{C}_{11}\text{H}_8\text{NO}_2)_2\text{Ca} + 2\text{H}_2\text{O}$ , the silver salt,  $\text{C}_{11}\text{H}_8\text{NO}_2\text{Ag}$ , and the copper salt,  $(\text{C}_{11}\text{H}_8\text{NO}_2)_2\text{Cu} + 6\text{H}_2\text{O}$ , are obtained from the ammonium salt by precipitation; they are crystalline.

*Metaquinaldinecarboxylic Acid.*—It is necessary to use a larger excess of paraldehyde and of hydrochloric acid, and the mixture requires heating. The free acid is prepared from the crystalline hydrochloride as above. The following salts are described:  $\text{C}_{11}\text{H}_9\text{NO}_2\cdot\text{HCl} + \text{H}_2\text{O}$ ; the abnormal platinum salt,  $4(\text{C}_{11}\text{H}_9\text{NO}_2\cdot\text{HCl})\cdot\text{PtCl}_4$ , also  $(\text{C}_{11}\text{H}_9\text{NO}_2)_2\cdot\text{H}_2\text{Cr}_2\text{O}_7$ ;  $(\text{C}_{11}\text{H}_8\text{NO}_2)_2\text{Ca} + 2\text{H}_2\text{O}$ ;  $(\text{C}_{11}\text{H}_8\text{NO}_2)\text{Ag}$ ; and  $(\text{C}_{11}\text{H}_8\text{NO}_2)_2\text{Cu} + 3\text{H}_2\text{O}$ .

*Orthoquinaldinecarboxylic Acid.*—Here an excess of paraldehyde must be avoided. The free acid melts at  $151^\circ$ , and is decidedly soluble in cold water; it crystallises from hot water with  $\frac{1}{2}$  mol.  $\text{H}_2\text{O}$ , which it loses at  $100^\circ$ . The hydrochloride is very soluble in water, and is not reprecipitated by strong hydrochloric acid; the platinochloride,  $(\text{C}_{11}\text{H}_9\text{NO}_2)_2\cdot\text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}$ , is easily soluble in hot water; the chromate is also soluble in hot water. The silver, calcium, and copper salts,  $(\text{C}_{11}\text{H}_8\text{NO}_2)_2\text{Cu}\frac{1}{2}\text{H}_2\text{O}$ , are described. H. B.

**Conine.** By A. W. HOFMANN (*Ber.*, **17**, 825—833).—Conine hydrochloride, distilled with zinc-dust, does not yield an amine, viz., octylamine, but one of the pyridine bases,  $\text{C}_8\text{H}_{11}\text{N}$ , *conyrine*, having nearly the same boiling point ( $166$ — $168^\circ$ ) as conine, from which it is separated by conversion into the hydrochloride; all its salts, with the exception of the platinochloride, are very soluble in water. Methyl iodide combines at ordinary temperatures with conyrine to form the iodide of an ammonium base. By the action of silver chloride,

the chloride and thence the platinochloride were prepared; it is  $(C_8H_{11}N, MeCl)_2, PtCl_4$ . Conyryne boils lower than other known bases of the same formula; moreover, it is distinguished by a blue fluorescence and the absence of any tendency to polymerise; with potassium permanganate, it yields a pyridinecarboxylic acid, viz., picolinic acid. Conine also yields conyryne when distilled with zinc chloride. According to Skraup and Cobenzl, picolinic acid contains the nitrogen and carboxyl groups in the ortho-position; conyryne will then be orthopropylpyridine, and conine itself hexahydrated propylpyridine or orthopropylpiperidine.

The reconversion of conyryne into conine is easily effected by heating it with hydriodic acid at 230—300°. Natural conine, and conine regenerated from conyryne have exactly the same physiological action. Conyryne is not so poisonous and acts more like a narcotic.

The synthesis of conine is thus simplified. Ladenburg has prepared ethylpyridine by methods used for obtaining the substituted anilines, and it is probable that conyryne or conine will be formed by the action of isopropyl iodide on pyridine or piperidine at a high temperature. H. B.

**Thebaine.** By W. C. HOWARD (*Ber.*, 17, 527—533).—*Bromothebaine tetrabromide*,  $C_{19}H_{20}Br, NO_3, Br_4$ , is obtained as a yellowish-red precipitate by adding an excess of bromine-water to a dilute solution of thebaine in hydrobromic acid.

*Bromothebaine*,  $C_{19}H_{20}BrNO_3$ , is prepared by adding bromine-water to the hydrobromic acid solution of thebaine as long as a precipitate is formed, filtering, and adding ammonia to the filtrate, when it forms a precipitate, which is at first reddish, but finally becomes blue.

*Morphothebaine*,  $C_{17}H_{17}NO_3$ .—The acid hydrochloride or hydrobromide of this base is obtained by heating thebaine with concentrated hydrochloric or hydrobromic acid in sealed tubes at 80—90°. The base is thrown down from solutions of its salts by caustic alkalis, carbonates of the alkali metals, or ammonia, as a greyish-blue precipitate, soluble in excess of caustic alkalis. It is soluble in alcohol and ether, also in benzene, from which it crystallises in well-defined crystals melting at 190—191°. *Morphothebaine hydrochloride*,



obtained by treating the acid hydrochloride with alcohol, forms small shining crystals, insoluble in alcohol, but soluble in water. The *hydrobromide* resembles the hydrochloride. The *nitrate*,



obtained by treating the solution of the hydrochloride with silver nitrate; it forms white small crystals. The *sulphate*,



prepared in a similar manner, crystallises from its aqueous solutions in monoclinic crystals. *Acetomorphothebaine*,  $C_{17}H_{16}NO_3Ac$ , prepared by heating morphothebaine hydrobromide with acetic anhydride and sodium acetate, crystallises from alcohol in shining scales which melt



at 183°. The solutions of morphothebaine hydrochloride are precipitated by platinic and auric chlorides, by potassium ferrocyanide, potassic bismuthic iodide, ammonium molybdate, potassic mercuric iodide, and potassic chromate.

Phosphorus pentachloride reacts with thebaine, yielding a compound containing no chlorine, proving the absence of a hydroxyl-group in the same. *Thebaine methiodide* is obtained by heating a solution of thebaine in methyl alcohol with methyl iodide; crystallised from alcohol, it gives crystals having the composition  $C_{19}H_{21}NO_3, MeI, EtHO$ . *Thebaine ethiodide*,  $C_{19}H_{21}NO_3, EtI$ , obtained like the above, crystallises from alcohol in fine needles. *Thebaine ethyl chloride*, formed by decomposing the iodide with silver chloride, crystallises from a mixture of alcohol and benzene in slender white needles.

*Thebaine benzyl chloride* crystallises in small nodules.

P. P. B.

**Synthetical Piperidine.** By A. LADENBURG and C. F. ROTH (*Ber.*, 17, 513—515).—One of the authors has already shown that by the action of sodium on an alcoholic solution of pyridine it is converted into a hexahydro-base, very nearly resembling piperidine. The authors have compared these two bases carefully with one another, and have established their identity.

P. P. B.

**Putrefactive Alkaloids.** By L. BRIEGER (*Ber.*, 17, 516—517).—The author proposes the name *neuridine* for the alkaloid  $C_5H_{14}N_2$ , described by him (*Abstr.*, 1883, 1159), since it yields trimethylamine when boiled with potassium hydroxide. Atropine stops the poisonous action of the alkaloid  $C_5H_{11}N$ , which contracts the pupil when introduced into the eye. The author is of opinion that this poisonous alkaloid is *trimethylvinylammonium hydroxide*, and this is supported by the analysis and chemical and physical characters of its platinochlorides, also by the physiological action of the trimethylvinylammonium hydroxide.

Commercial neurine appears to contain two bases, one having the formula  $C_5H_{11}N$ , and forming sparingly soluble platino- and aurochlorides, and another  $C_5H_{14}NO = Me_3N(OH).C_2H_4.OH$ , *trimethylhydroxyethylammonium hydroxide*, forming an easily soluble platinochloride.

P. P. B.

## Physiological Chemistry.

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**Researches on the Development and Nourishment of the Silkworm.** By O. KELLNER, T. SAKO, and J. SAWANO (*Bied. Centr.*, 1884, 235—240).—Silkworms were fed with weighed quantities of mulberry leaves, which were given during all periods of growth, those periods being (1) a week from the hatching of the egg; (2) May 6—12; (3) May 12—19; (4) 19—26; (5) May 26—June 3, when the chrysalis state was assumed; (6) June 6, when the cocoon was completed; (7) June 22, when the butterfly emerged. It was

during the 4th period that the excrement of 1000 worms was examined, and found to contain 2.49 per cent. of uric acid, which fell to 1.31 per cent. in the 6th; but little ammonia was found, and no urea. Of the food given the worms only consumed about  $\frac{1}{6}$ — $\frac{1}{5}$ , and of the digested matter the nutrient ratio was as follows:—

Period...	1	2	3	4	5
N.R. ....	1:1.85	1:2.13	1:1.94	1:2.14	1:1.45

But little of the fibrous matter could be digested, but the albumin and fat were digested to an extent surpassed only by ruminants. The following table shows the composition of the worm, &c., at different ages:—

	Newly hatched.	Period 1.	Period 2.	Period 3.	Period 4.
Water .....	75.94	84.10	85.68	86.92	87.81
<i>In 100 dry matter.</i>					
Protein less chitin .....	75.58	75.42	73.26	72.52	72.23
Chitin .....			5.32	5.46	5.40
Fat .....	16.20	8.72	10.73	12.55	11.47
Ash .....	6.40	9.05	8.98	9.48	9.32
Undetermined .....	1.82	6.81	1.79	—	1.58
Total nitrogen .....	12.09	12.07	12.04	11.93	11.88
Albuminoid and peptin nitrogen	11.39	11.06	10.42	9.81	9.94
Chitin nitrogen .....			0.32	0.33	0.32
Nitrogen in undetermined compounds* .....	0.71	1.01	1.30	1.79	1.62
Ditto in per cent. of total N.	5.80	8.30	10.80	15.00	13.30

	Period 5.	Empty cocoon.	Pupa.	Butterfly.
Water .....	80.33	12.50	78.89	71.77
<i>For 100 dry matter.</i>				
Protein less chitin .....	59.16	98.82	55.81	56.58
Chitin .....	4.77	—	3.89	7.38
Fat .....	16.31	0.01	28.17	32.01
Ash .....	6.06	1.18	5.62	3.94
Undetermined .....	13.70	—	6.51	0.10
Total nitrogen .....	9.75	17.97	9.16	9.49
Albuminoid and peptin nitrogen .....	8.11	—	5.68	8.18
Chitin nitrogen .....	0.29	—	0.23	0.44
Nitrogen in undetermined compounds* .....	1.35	—	3.25	0.87
Ditto in per cent. of total N.	13.80	—	35.50	9.20

\* Precipitated by phosphotungstic acid.

The remarkably rapid growth of the worm is exemplified by the figures in the subjoined table:—

	Ratio of live weight. Weight of new-hatched worm = 1.	Ratio of dry weight.
Period 1.....	11·40	7·70
„ 2.....	61·80	37·40
„ 3.....	275·50	152·20
„ 4.....	1241·90	639·70
„ 5.....	5364·70	4457·70
Cocoon and pupa ....	2826·10	3468·50
Butterfly .....	1215·00	1450·70

From this it is evident that much of the increase in live weight is due to water, and from the previous table we learn that nearly one-half of the albuminoids in the worm are employed in the formation of the silk of the cocoon.

Passing on to the amount of the food constituents digested, the following will show all that is necessary on this point:—

Periods .....	1	2	3	4	5	Average.
Dry matter.....	29·4	28·9	27·2	37·8	63·3	56·6
Organic matter.....	27·5	27·0	25·3	35·7	61·9	55·0
Crude protein .....	45·0	58·1	51·5	79·7	87·1	83·8
Albumin .....	68·8	70·0	45·6	71·4	75·6	73·5
Fat .....	20·0	23·4	34·6	42·3	—	—
Potash.....	—	—	—	2·1	3·5	—
Lime .....	—	—	—	23·7	18·7	—
Magnesia.....	—	—	—	34·5	33·8	—
Phosphoric acid .....	—	—	—	63·2	25·9	—

In the 5th period there was an addition to the fat, which was in excess of that contained in the food, and this excess could not have been produced by the decomposition of albumin, by reason of insufficiency, consequently we must suppose that some non-nitrogenous matter other than fat had been converted into this compound.

E. W. P.

**Urine of Cows and Sheep.** By E. ZACHAREWICZ (*Ann. Agronomiques*, 10, 177—183).—The author has estimated the urea in the urine of cattle and sheep under varying conditions of food and treatment. Esbach's ureometer-tube was employed, with Kraup's solution of sodium hypobromite.

The mean proportion of urea found in sheeps' urine was 20 grams per litre, and supposing a sheep to void 1 litre of urine per day, the urea excreted per annum would be 7·3 kilos. A very fat sheep excretes an unusually large quantity of urea, and a sheep in poor condition and bad health less than the average.

The urine of four cows receiving food of known composition was examined on June 15, July 13, and August 24, the mean proportions of urea being 21.14, 26.35, 14.80 grams per litre respectively for the three dates mentioned. The great falling off in August is due to the change of food, for whilst in August the cows received maize and cotton-cake only, in June and July they had cotton-cake, hay, straw, lucerne, and trifolium. The mean results give about 20 grams urea per litre, and reckoning with Boussingault 9 litres of urine per day, the total quantity of nitrogen excreted in the form of urea will be 28—30 kilos. per annum per cow. The nutrient ratio of the three foods given was in June, 1 : 3.9; July, 1 : 5; and August, 1 : 8.8. By analysis of the milk, the author shows that the highly nitrogenous diet of July did not cause any corresponding increase of casein in the milk, but that the excess of nitrogen was excreted as urea in the urine.

J. M. H. M.

**Influence of Movement on the Secretion of Milk.** By H. MUNK (*Bied. Centr.*, 1884, 232).—Most of the writers on the subject have stated that movement is detrimental to the secretion of milk. Fleischmann, however, found that the reduction in quantity is but slight, and is fully compensated for by the increased yield of solids. To settle this question, the author experimented with 30 cows, and finds that when the cows had half an hour's exercise during the day, the total quantity of milk as well as the fat and casein increased, but much exercise was detrimental to the yield; when the cows are on grass, their increased appetite and the abundance of food fully compensates for any loss incurred by the motion required to obtain that food. It is therefore advisable that milch-cows when being stall-fed, should have daily exercise.

E. W. P.

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## Chemistry of Vegetable Physiology and Agriculture.

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**A Concentrated Nutritive Fluid for Plants.** By W. KNOP (*Landw. Versuchs-Stat.*, **30**, 292—294).—The author who is engaged in experiments on the absorption of various acids and bases by the roots of plants, recommends in this paper the use of a liquid fertiliser of his own invention, which, being of known composition and concentration, can be readily diluted to suit the requirements of the experimentalist.

There are two solutions, viz., No. 1—

205 grams of magnesium sulphate = 100 grams of the anhydrous salt = 33.33 MgO + 66.67 SO<sub>3</sub> in 3.5 litres of water.

No. 2 solution—

400 grams calcium nitrate	= 136.58 CaO + 263.42 N <sub>2</sub> O <sub>5</sub> .
100    ,,   potassium nitrate	= 46.58 K <sub>2</sub> O + 43.52 N <sub>2</sub> O <sub>5</sub> .

100 grams potassium phosphate =  $34\cdot63 \text{ K}_2\text{O} + 52\cdot22 \text{ P}_2\text{O}_5 + 13\cdot15 \text{ H}_2\text{O}$

dissolved in the same quantity of water, 3·5 litres.

For use, he suggests mixing 100 c.c. of each, and making up to 10 litres, each litre would then contain—

Water of combination.....	0·0377	
Potash .....	0·2320	
Lime .....	0·3903	
Magnesia .....	0·0952	
Combined phosphoric acid..	0·1491	
Sulphuric acid.....	0·1905	
Nitric acid .....	0·9052	
Free phosphoric acid .....	0·0746	J. F.

**Influence of Light and Heat on Plants.** By HELLRIEGEL (*Bied. Centr.*, 1884, 240—253).—A continuation of the author's researches (this vol., 855). As it was thought impossible that plants growing in glass-houses could obtain light of an intensity equal to that which they would receive outside, the results of experiments conducted under cover would not be perfectly trustworthy; the author therefore arranged that the plants experimented on should be exposed to the free air in fine weather, but removed under shelter when bad weather occurred; as a proof that the new arrangements made considerable differences to those obtained under the old method, the results of experiments are quoted, which show that not only was the total yield of barley greater, but that the weight also of the grains harvested was heavier in free air and direct sunlight than in diffused light. Barley plants were grown under coloured glass—cobalt glass, which allowed of the passage of the red and green rays as well as of the violet, and yellow carbon glass in which the violet and blue were extinguished,—with this result, that under the influence of the blue light less ash and more organic matter were produced than under the yellow. Those under the blue glass grew well, whilst those under the yellow seemed to be retarded in their growth, and when shaded were long in the internodes, and the leaves were thin and delicate. Taking this experiment in conjunction with another somewhat similar one, the author comes to the conclusion that plants are not very sensitive to moderate changes in the composition of the light which falls on them, consequently that the light as altered by the roof and walls of a glass-house cannot have any serious detrimental influence on the plants growing in that house.

In order that land should produce a maximum crop, it is necessary that each plant should have assigned to it a definite volume of porous soil for the proper development of its roots; that there be a sufficiency of moisture, enough of available nutriment, and finally a definite quantity of light and heat. Of all these factors which make up the fertility of a soil, the last two are not under the guidance of man. The author, therefore, in 1870, tried to estimate the influence exerted by the light and heat, but failed; the account of the experiments is given in detail. In a second series, barley and peas were grown in

glass vessels of two sizes, and the plants as soon as they appeared were shaded by cylinders of cardboard placed vertically, so that no side light could reach the plants; these cylinders were of different sizes, some being broader than the vessel holding the soil, others of the same diameter; some broader above than below, and *vice versâ*; the results obtained were unexpected—the stems grew lengthy and rapidly, being thin and weak; the lower leaves were pale; those of the peas reddish; it appears, then, that under the influence of the shades the growth is somewhat abnormal, and this is the more marked the narrower the shading cylinder; under all these disadvantages, however, the plants fruited, but under all conditions those plants growing unshaded produced the most fruit, and, as the cylinder narrowed, the yield of grain decreased, whilst the chaff and the straw (peas excepted) increased. The author had previously believed that when the plants grew freely in the field, it was the light which fell on the crown of the plants which influenced their growth, as so much of the rest of the plant was shaded. It was also remarked that under the medium-sized shades with the upper opening of the same size as the pots, although the other conditions were so various, yet the amount of dry matter in the plants was approximately the same.

As regards the warmth necessary for the proper growth and ripening of plants, the experiments are detailed very fully, but it will suffice to state the results obtained. For the growth of four-rowed barley, the average daily temperature during the first half of the period of vegetation must be about  $15^{\circ}$ , in the latter half when the blossom forms, &c., the average must be  $17-18^{\circ}$ , and the average of the whole season  $16^{\circ}$ . The average of the mid-day during the first period must be  $20^{\circ}$ , during the second period about  $25^{\circ}$ , the average during the whole season about  $21^{\circ}$ .

E. W. P.

**Relation between Chemical Metamorphosis and Transformation of Forces during the Germination of Seeds.** By H. ROEDWALD (*Ann. Agronomiques*, 10, 236—237).—Two equal weighed quantities of clover-seeds are taken, and one of them used for the determination of total dry solids; the other portion is moistened and allowed to germinate for 5 or 9 days, the soluble matters formed during germination being absorbed by a layer of glass wool. The total dry solid matter in the germinated seed is then ascertained and ultimate analyses are made of this dry matter and of that from the corresponding quantity of ungerminated seed. The calorific power of 1 gram of dry matter from each source is next found by combustion in a calorimeter with a deflagrating mixture composed of potassium chlorate, antimony sulphide, and cane-sugar—the sum of the heat disengaged by combustion of the flux and dissociation of the potassium chlorate being deducted from the total amount obtained. Experiments conducted in this way show that 1 gram of the dry matter consumed by respiration disengages 2564 calories and 5938 calories during a germination of 5 and 9 days respectively. The matter which disappears during the first five days is of sensibly the same composition as starch, and outside of the seed would be capable of disengaging 4479 calories per gram by combus-



tion. The matter oxidised during the nine days corresponds in composition with a mixture of 60 per cent. starch and 40 per cent. fat, and is theoretically capable of disengaging 6641 calories per gram.

There is therefore a considerable amount of force absorbed during germination.

J. M. H. M.

**Comparative Growth of Peas and Maize in Mineral and Organic Solutions.** By V. JODIN (*Ann. Agronomiques*, 10, 193—215).—In this paper are collected the details of experiments made some years ago on the culture of peas and maize in certain artificial solutions.

1. *Organic solution* consisting of a certain weight of dried and powdered pea plants (seed and straw) inclosed in a porous cell placed in a porcelain crucible full of water, so that gradual exosmosis of the soluble matter took place through the walls of the cell. The crucible was furnished with a lid pierced with two holes to admit the stems of the pea and maize plants. The weighed seeds were allowed to germinate in water or in soil, and the plants then transferred to the artificial solution. Growth took place in both cases, that of the maize being much more luxuriant than that of the pea—the dried crop from the maize seed being 29.38 times the weight of the seed, and that of the pea 4.18. Determinations were made of nitrogen and minerals contained in these crops, in the manure supplied, and in the residual liquid, and from these figures the proportions of nutritive substances in the manure utilised by the growing plants were calculated.

2. *Mineral Solution*.—This contained all the minerals of the preceding organic solution, and in about the same proportions, but the nitrogen was supplied as a nitrate. The experiments were conducted as with the preceding solution, and the amount of growth was about the same.

3. *Mixed Solution*.—A quantity of the powdered pea-manure was placed in a funnel provided with a stop-cock, and moistened with water. From time to time the water was allowed to run through into a flask and was again poured into the funnel. This treatment was prolonged for about a year, when the residue in the funnel was only a fifth of its original weight. The solution thus obtained (A) was employed alone in some of the cultivations, and in others was mixed with a mineral solution (B) made by dissolving the ash of an equal weight of dried pea plant in the smallest possible quantity of nitric acid, and diluting with water. The solution B was also employed alone in some of the experiments, and the results of the three methods go to show that in the mixture of the solutions A and B each produced its proportional effect, and no increase of crop was obtained by the mixture. Solution A gave very small and feeble plants, whilst those grown in B were comparatively luxuriant and robust.

The results of all the experiments, which are given in great detail, go to show that the plants derived no benefit from the decaying organic matter of the manure, except in so far as the nitrogen was gradually transformed by putrefaction and fermentation into the mineral forms of ammonia and nitric acid. In all cases in which estimations were made, there was a loss of nitrogen—often amounting to 50 per cent. of that in the seed and manure.

J. M. H. M.

**Function of Tannin in Vegetable Cells.** By W. GARDINER (*Ann. Agronomiques*, 10, 188—189; from *Proc. Cambridge Phil. Soc.*, IV).—By means of Rose's reagent, the author has made some microchemical observations on the occurrence of tannin in vegetable cells. Rose's reagent consists of ammonium molybdate dissolved in a saturated solution of ammonium chloride, and strikes a red colour with tannin glucosides and tannic acid. An excess of the reagent produces a voluminous precipitate, if the tannin be a glucoside. Tannins are very abundant in the motor tissue of the sensitive plant and similar tissues, and there is possibly some connection between the presence of tannin and the irritability of the tissue. It is probable that tannin is one of the ultimate products of the metamorphosis of immediate principles, that it is not utilized by the plant, and that its disappearance when once deposited is doubtful. J. M. H. M.

**Acidity of Cell Sap.** By G. KRAUS (*Ann. Agronomiques*, 10, 238—240).—By means of dilute (0.1 per cent.) standard solution of sodium hydroxide, the author has determined the total acidity of the cell sap contained in the different organs of growing plants in various circumstances. The leaves are the most acid parts of ordinary herbs and shrubs, the roots the least. This rule is reversed in the *Crassulaceæ*. The wood and bark are more acid than the pith. In many leaves, the acidity often increases from the tip to the base. The acidity of a stem generally increases with the age, *i.e.*, from above downwards, but in some cases, young lupins for example, it remains constant for some time. The petals of the *Boraginaceæ*, red when young, are more acid than when blue and full grown. In an organ undergoing geotropic curvature, the acidity diminishes on the convex side. When a plant germinates in darkness the acids increase; they diminish when it is transported into the light, but subsequently increase. A plant may grow in the dark without any increase of acidity. It has been known for some time that the leaves of the *Crassulaceæ* become very acid during the night, but lose their acidity in the day. The author shows that this periodicity is a general phenomenon differing only in intensity in different plants, and directly dependent on the illumination. Not only can the acidity be caused to increase by shading the plants during the day, but a local accumulation or development of acid can be produced by darkening a particular leaf or part of a leaf. The red rays of the spectrum are more potent than the blue in relation to this phenomenon. In an atmosphere of carbonic anhydride or hydrogen, acids are not formed during the night nor are they decomposed during the day, so that these changes are not related to the diurnal assimilation of carbon. In the night, when the acidity is greatest, the quantity of glucose is least, and during the day as the acids diminish so the glucose increases.

J. M. H. M.

**"Butter Beans," a new Variety of Fatty Seeds.** By F. v. HÖHNEL and J. WOLFBauer (*Dingl. polyt. J.*, 252, 333—337).—During the last few months, fatty seeds of remarkable size have been brought into commerce by way of Marseilles and Trieste consisting of the split embryo of endospermless seeds, which belong to the *Vateria*

*indica*, a tree growing in India (especially Malabar), whence large quantities of vegetable fat (Malabar tallow) have been recently imported into Europe. The seeds are brought into the market in a decayed condition, the fruits being gathered triennially and not as they fall from the trees. The seeds have an aromatic and bitter taste, and a faint aromatic odour. Examined under the microscope, they appear to be made up of thin isodiametric parenchyma cells, the contents of which are composed of three ingredients: (1) yellow hyaline, or fine-grained masses of albuminous bodies (protoplasm) insoluble in boiling alcohol; (2) fatty substances, which are colourless, hyaloid, and crystalline, at places forming masses which, in consequence of the decay of the seeds, are quite separate from the yellow albumin; (3) numerous starch granules (to the extent of from 15—20 per cent.). The seeds of the *Vateria indica* when dried in the air contain 49·21 per cent. of a greenish-yellow solid fat characterised by its agreeable slightly balsamic odour. The fat resembles mutton tallow in hardness and viscosity, has a sp. gr. of 0·915 at 15° and melts at 42°. It consists of 81 per cent. neutral fatty acid glycerides, separated from the products of saponification melt at 56·6°, solidify at 54·8°, and represent a mixture of oleic acid and solid fatty acids melting at 63·8°, and constituting 60 per cent. of the total weight of vegetable fat.

D. B.

**Action of Hydroxylamine Salts on Plants.** By V. MEYER and E. SCHULZE (*Ber.*, 17, 1554—1558).—The position which hydroxylamine occupies between the two nitrogenous foods of plants, ammonia and nitric acid, and its great chemical activity as compared with the inertness of these food-stuffs, seem to point to a probable formation of hydroxylamine in the organisms of plants, and to its playing an important part in the assimilation of starchy and other matters and the formation of albuminoids.

With the view of throwing some light on this subject, the authors have made some experiments on nourishing maize and barley by means of artificially prepared food solutions. One solution contained in 1 litre, 0·25 gram  $\text{CaSO}_4$ , 0·25 gram  $\text{MgSO}_4$ , 0·5 gram  $\text{KH}_2\text{PO}_4$ , 0·15 gram  $\text{NaCl}$ , and 0·80 gram  $\text{Ca}(\text{NO}_3)_2$ , and a trace of ferric chloride. In the other solutions, the calcium nitrate was replaced by its equivalent proportion of ammonium sulphate, hydroxylamine hydrochloride, or hydroxylamine sulphate respectively. The plants thrived well in the nitrate solution, moderately well in the ammoniacal solution, but very soon died in each of the hydroxylamine solutions. In pure water, they lived and put forth leaves long after those in the hydroxylamine solutions were dead. It is thus clear that hydroxylamine acts on plants as a poison, and this is confirmed by the fact that a very little hydroxylamine salt added to a solution of gelatin and to hay extract acted antiseptically, preventing the formation of mould, &c. It is still possible that hydroxylamine may be formed in plants as a transition-product and yet act as a poison when taken up by the roots, just as peptone acts as a poison when introduced into the veins of animals.

L. T. T.

**Importance of Silicic Acid in the Culture of Oats.** By C. KREUZHAGE and E. WOLFF (*Landw. Versuchs-Stat.*, 30, 161—198).—The experiments described were carried out at the experimental station of Hohenheim in water culture, the silicic acid was obtained by treating chemically pure silica with warm caustic potash solution and neutralising the potash by free nitric acid previously added to a nutritive solution employed at Hohenheim in agricultural experiments—the silicic acid was thus left in a free state dissolved in the solution containing the other fertilising matters.

Three sets of experiments were made, one without silica, and the others with weak and strong solutions of silica.

The details are voluminous, but summarised show that the absorption of silica greatly assists the assimilation of other plant foods, and that plants to which it is supplied show a decidedly more healthy development of grain and straw than others not so treated. Previous experiments at the same station had shown that phosphoric acid acted in a similar way (assisting the assimilation of ordinary plant foods); the authors therefore ask the question if it is possible to replace phosphoric by silicic acid in the composition of artificial manures. Attempts in this direction have been made by manure manufacturers but without success, due, the authors think, to the use of the silica in an unsuitable form; its success depends greatly on its correct preparation, and extensive experiments are desirable; they should be made under normal agricultural conditions, experiments in water culture not being decisive, as plants absorb more nutriment from the solutions employed than if the same matters are applied in ordinary culture in earth.

The authors doubt the possibility of silicic acid replacing phosphoric in manures, but they look forward to a combination of both, which will yield excellent results in the culture of the Graminaceæ.

J. F.

**Feeding Cattle on Lupines.** By L. SEEING (*Bied. Centr.*, 1884, 273).—The author has been successful in feeding cattle with lupines freed from the bitter principle.

E. W. P.

**Cultivation of Sugar Beet and other Roots.** By MÄRCKER and others (*Bied. Centr.*, 1884, 262—271).—Märcker in his experiments found "Little Wanzlebener original" produced the heaviest yield of sugar per morgen, whilst "Dippe's Wanzlebener" had the highest quotient of purity. Scholz obtains most sugar from "Eigene Schlesische," but the highest quotient was from Little Wanzlebener in humous soil. F. Bastian grew roots on sandy loam and manured with dung, dung and super, and dung mixed with ammonium superphosphate; the heaviest crop of roots was produced by the last mixture, and the quotient of purity was also the highest, viz., 87. The analyses of roots made by Pagnoul are of interest, as they show that large quantities of salts and nitrates are retained in the ripened root; in the roots manured with dung, there was found of salts 1·066 per cent.; of nitrate 0·728; or referred to 100 parts of sugar, 24·12 and 16·47 respectively; this is the more interesting, as it shows the formation of nitrate when dung decomposes; the presence of salts causes a rapid

development of leaves, which in their turn cause the nitrate which the plant when manured with nitre had absorbed to be decomposed. Pagnoul further experimented on the influence of light on the decomposition of nitre in the plant, by raising the plants under glass, some of which was transparent, the rest blackened. In the shade there was much more nitrate undecomposed, showing that the activity of leaf-growth was necessary for the proper decomposition of this compound; consequently, when the leaf-growth is rapid and ripening occurs early, the leaves produce sugar in those months when the days are long and the sky clear, whilst the late ripening kinds produce more sugar because the growth of the leaves is carried on into autumn when the weather is warm and moist.

B. Corenwinder grew beet in pots filled with sand to which manures containing no carbon in any form were added, also in pots containing carbonaceous manures, and in the field, with the result that the beet leaves were capable of obtaining all necessary carbon for their growth; in fact, the weight of the crop grown on the sand was very little less than that grown in the field, whilst the percentage of sugar was much higher. The other articles on the subject are of no chemical interest.

E. W. P.

**Researches on the Sugar-cane.** By W. KNOP (*Landw. Versuchs-Stat.*, 30, 277—287).—Several samples of sugar-cane which had been attacked by a fungoid growth were sent to the author from Pernambuco; this disease has caused great injury to the plantations, but the author is unable to propose a remedy, and thinks the subject should be studied on the spot. The paper contains remarks of interest on the analysis of the cane, and of the soil on which it was grown, samples of which were also sent to him. The analyses Nos. 1 and 2 are of the ash of diseased canes, No. 3 of sound. The author considers that the differences do not exceed those observed in the ashes of other grasses at various stages of their growth.

	No. 1.	No. 2.	No. 3.
Silicic acid.....	34·5	32·7	38·8
Lime .....	2·5	7·5	4·0
Magnesia.....	6·8	14·1	7·5
Phosphoric acid.....	3·4	4·3	4·0
Sulphuric acid .....	3·4	3·3	3·2
Chlorine.....	12·3	9·6	10·6
Potash.....	36·7	28·0	30·3
Soda .....	0·4	0·5	1·6

He draws special attention to the large amount of potash present, more than sufficient to saturate the acids and chlorine, and leave a considerable surplus. Manganese and iron were present but in small quantities, and in presence of phosphoric acid were not estimated.

The soil consists of decomposed quartz and quartzite, containing iron and manganese; its mechanical condition showed a proportion of 53 per cent. of fine clay to 47 per cent. of different grades of sand and gravel.

J. F.

**Volume-weight of some Manures.** By V. MAGERSTEIN (*Bied. Centr.*, 1834, 281).

Manure.	1 hectol weighs	Max. of moisture absorbed after three days' exposure to moist air.	Volume increase, per cent.
	kilos.	kilos. per hectol.	
Potassium sulphate .....	128	0·66	5·0
Kainite .....	82	0·69	7·5
Chili saltpetre .....	105	1·00	0·5
Ammonium sulphate .....	84	2·00	6·5
Lime (dust) .....	106	1·66	1·3
Calcium sulphate .....	77	1·60	2·0
Potashes .....	41	0·10	1·0
Coal ashes .....	69	2·33	1·5
Raw bone meal .....	85	1·00	6·5
Steamed bone meal .....	81	2·50	8·3
Baker guano .....	112	6·00	4·0
Bone superphosphate .....	76	1·33	2·0
Sodium superphosphate .....	82	3·33	3·0
Peruvian superphosphate .....	61	2·00	0·6
Baker superphosphate .....	92	3·30	6·5
Mejillones superphosphate .....	90	2·33	5·0
Ammonium " .....	72	5·33	8·0
Dissolved flesh meal .....	76	4·30	16·0
Blood meal .....	67	6·67	12·0
Liquid manure (cows') .....	102	—	—

E. W. P.

**Report on Experiments on Manuring Grain.** By EMMERLING, LOGES, and METGER (*Bied. Centr.*, 1884, 217—227).—These experiments, made in 1882, are a continuation of those made in 1880—81 (*Abstr.*, 1881, 309; 1882, 333; 1884, 211). The season was good, although the harvesting suffered somewhat by storms; the manures included superphosphate, precipitated phosphate, blood, ammonia, &c. The results on the crops, barley, oats, on the different classes of soil in the neighbourhood of Kiel are fully given, as also the analyses of the soils. The experiments on marsh land show a loss when precipitated phosphates are used, because the superphosphate penetrates deeply, rapidly and more completely into such a soil than does the other manure. Ammonia in all cases brought an increase, but that increase was insufficient to pay for the extra cost; but as for Chili saltpetre there was, beside a gain in crops, also an increase sufficient to pay expenses. The combination of phosphate with ammonia always brought an increased yield, and although there was no direct financial gain, yet a sufficient quantity of manure was left in the soil for the succeeding crop, so saving something in the succeeding season. Chili saltpetre with phosphoric acid on loam and sandy loams gave excellent results, but when the soil was deficient in lime, the precipitated phosphates worked well. Finally, the authors show that in the loamy soils of Holstein the value of superphosphate compared with pre-

cipitated phosphate is 40 : 21 (eliminating the action of the nitrogen); in the previous season of 1880, which was bad, this value came out 40 : 22, the money ratio of the two being 40 : 32, consequently in such districts the former material is better than the latter. As regards bone meal and blood, it is only in those soils wanting lime that steamed bones take first rank.

E. W. P.

### Loss of Nitrogen by Organic Matters during Putrefaction.

By A. MORGEN (*Landw. Versuchs-Stat.*, **30**, 199—216).—This subject has been studied by many chemists, and its importance to agriculture fully admitted. Different processes have been suggested to prevent the loss. Lawes and Gilbert proposed the addition of burned earth to the decaying substance, König and Kiesow of ordinary garden soil unburned, and the same experimenters recommended gypsum.

The author undertook a series of experiments on the subject, and arrived at the following conclusions:—The loss of nitrogen during putrefaction of nitrogenous organic substances is large and constant; its amount greatly depends on the mechanical condition of the substance; if loose, porous, and moist, it loses much more than if densely packed and moderately dry. The loss he attributes to a process of oxidation and nitrification, free nitrogen being set free simultaneously with the formation of nitrites and nitrates. As a preventative he tried the addition of clay, without success; 5 per cent. of gypsum diminished the loss very materially, but the greatest success was obtained by the use of 5—10 per cent. of kainite, which in all cases reduced the loss to a very small amount, and in some instances prevented any loss whatever. The reason that this result was obtained is not understood, but the author promises to investigate the matter.

J. F.

### Retrogression of Superphosphates.

By W. KNOP (*Landw. Versuchs-Stat.*, **30**, 287—291).—The author first draws attention to the discovery of Märcker, that samples of commercial superphosphate kept in glass-stoppered bottles do not retrograde, but that samples of the same in tin boxes show a gradual return from the soluble to the insoluble form. The general opinion is that the retrogression is due to the presence of salts of iron and alumina, but the author thinks there are other causes not yet fully investigated. In the preparation of a liquid fertiliser, consisting of a solution of calcium nitrate, potassium nitrate, and potassium phosphate, he found that after a time a pulverulent crystalline salt was deposited, which on analysis he found to be bibasic calcium phosphate, with variable amounts of combined water. Two specimens very carefully prepared were of the following composition:—

Sample A	.....	$\text{Ca}_2\text{H}_2\text{P}_2\text{O}_8 + \text{H}_2\text{O}$ .
Sample B	.....	$\text{Ca}_2\text{H}_2\text{P}_2\text{O}_8$ .

J. F.

## Analytical Chemistry.

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**An Indicator.** By A. GAWALOWSKI (*Bied. Centr.*, 1884, 286).—A mixture of an alcoholic solution of phenolphthaleïn with dimethylaniline orange is recommended as indicator in alkalimetry or acidimetry. The mixture is lemon-yellow when quite neutral, whilst when acid it is rose-red; when alkaline, deep-red. E. W. P.

**Analysis of Volatile Organic Sulphur-compounds.** By V. MEYER and O. STADLER (*Ber.*, 17, 1576—1577).—In the estimation of nitrogen in volatile compounds containing sulphur by Dumas' method, great care must be taken to carry on the combustion *very slowly*. If burned at all quickly, carbonic oxide is evolved, probably formed by the reduction of carbonic anhydride by sulphurous acid in the presence of heated metallic copper. A very volatile substance containing a large percentage of sulphur was analysed to ascertain whether nitrogen was also present, when the authors obtained a considerable quantity of permanent gas; this, however, was found to be carbonic oxide, and not nitrogen. Satisfactory results were obtained on performing the combustion very slowly. L. T. T.

**Examination of H. Grouven's Method of Nitrogen Estimation.** By U. KREUSLER and H. LANDOLT (*Landw. Versuchs-Stat.*, 30, 245—271).—This new method (*Abstr.*, 1883, 1028) is said to have many advantages over other processes, especially in analyses of manures and agricultural products. The Prussian Ministry of Agriculture appointed the authors to fully examine the method, and this paper is their report. They purchased two sets of apparatus from the holders of the patent, and carried out two sets of experiments, one at the Experimental Station of Poppelsdorf, the other at the Agricultural High School in Berlin, where the personal supervision of Dr. Grouven was in many cases available. It is unnecessary to say that the experiments were conducted with every precaution to ensure impartiality. In those at Poppelsdorf the results were controlled by the soda-lime process and sometimes volumetrically; those in Berlin were made with substances from the laboratory, previously carefully analysed or of known composition.

The details of each experiment are given; but the results were all unfavourable to the new method, and the reporters say that it requires numerous precautions, and in the end does not easily yield correct results. They admit that the apparatus is thoughtfully constructed, and that the principle of burning the substances in a current of superheated steam is good, but in its present state it is not likely to supersede other and better known methods. J. F.

**Detection and Estimation of Ammonia in Animal Liquids.** By J. LATSCHENBERGER (*Monatsh. Chem.*, 5, 129—154).—Numerous methods have been devised for the estimation of ammonia in animal



liquids, but so far with very inaccurate results. The author, as the result of a long investigation of many different processes, recommends the following method :—20 c.c. of a cold saturated solution of cupric sulphate is placed in a beaker of about 120 c.c. capacity, weighed, 20 c.c. of the liquid under investigation added, and the whole again weighed. The mixture is then carefully neutralised with baryta-water, washed into a litre flask, and water added to make up a litre. The liquid after filtration should be perfectly clear and colourless. The amount of ammonia in the liquid is now determined colorimetrically by means of Nessler's solution; a standard solution of ammonium chloride whose strength = 0.01 mgrm. of  $\text{NH}_3$  per c.c. being used for comparison. The results obtained show a very close agreement. The following table gives the mean results obtained :—

Liquid employed.	Per cent. of $\text{NH}_3$ .
Human urine, sp. gr., 1.021.....	0.05550
Dog's urine, sp. gr., 1.018 .....	0.08038
Cow's milk.....	0.02106
Ox blood.....	0.00781
Ox gall .....	0.00283

A. J. G.

**Apparatus for the Estimation of Carbonic Anhydride.** By R. BAUR (*J. pr. Chem.* [2], 29, 489—493).—The author claims that by means of the apparatus which has been patented in Germany he has obtained a quick and, for technical purposes, correct method of estimating carbonic anhydride volumetrically. A drawing of the apparatus is appended to the paper.

The apparatus consists of two parts, the generator and the gas-measuring tube. The generator is a bottle in which the carbonate is placed, together with a bulb containing acid. This bottle is connected by an india-rubber tube and a three-ways stopcock to the measuring tube. This stopcock allows of direct communication between the two parts, or between the air and either or both of the two parts. The calibrated measuring tube is placed vertically in a cylinder; the top is drawn out and, passing through an india-rubber stopper fixed on the top of the cylinder, is attached to the three-ways stopcock. The lower end is open, and by means of a cork support is fixed in the lower part of the cylinder, which is slightly restricted for the purpose. The stopper at the top of the cylinder is fitted with a funnel for admitting liquid into the space between the cylinder and the measuring tube, and the bottom is also closed with an india-rubber stopper and fitted with a stopcock. The author uses a liquid for filling the cylinder and measuring tube which absorbs very little carbonic acid, but he does not mention what this liquid is.

The process consists, after the apparatus has been proved to be air-tight, in filling the cylinder and measuring tube through the funnel with the liquid up to the zero mark, and at the same time preserving atmospheric pressure in both parts of the apparatus by means of the three-ways stopcock. The connection with the air is then closed, but made between the two parts of the apparatus, and the acid is poured

on the weighed carbonate in the generator. As the carbonic anhydride is generated the liquid sinks in the measuring tube, and to keep the pressure constant is run out by opening the stopcock at the bottom of the outer cylinder. To withdraw the carbonic acid dissolved in the liquid in the generator, the pressure in it is diminished for a time by continuing to withdraw the liquid from the outer cylinder. The level of the liquid in the two tubes is afterwards restored by pouring sufficient liquid in at the top of the outer tube, and the amount of carbonic anhydride read off, and correction made for atmospheric pressure and temperature. The form of the apparatus prevents rapid change of temperature, and by withdrawing the carbonic anhydride from the liquid in the generator, the absorption coefficient may for technical purposes be neglected.

A. B.

**Estimation of Morphine in Opium.** By V. PERGER (*J. pr. Chem.* [2], 29, 97—110).—The author has carefully examined the methods in ordinary use for the estimation of morphine in opium, as to their relative accuracy, making analyses of the same sample of opium by each method, and finds that they give most variable results. The methods in common use are Godeffroy's, Austrian Pharmacopœia, and Merk's.

*Godeffroy's method* is as follows:—10 grams of dry opium powder are mixed with 25 c.c. of hot water, and then pressed between folds of linen, this operation being repeated until the water is no longer coloured. The liquid is then boiled two or three times with 8 to 10 grams of slaked lime and filtered; ammonium chloride is added to the filtrate until after standing it smells of ammonia. The morphine crystallises out after 12—24 hours, and can be estimated by collecting it on a tared filter and washing it with dilute ammonia.

*The Austrian Pharmacopœia method* is as follows:—10 grams of dry powdered opium are treated with 90 grams of a mixture consisting of 140 grams of distilled water and 40 grams of hydrochloric acid (12·2 per cent.). The residue remaining after filtering and washing is weighed. If the opium be good, it should not exceed 4·5 grams. The filtrate is mixed with 20 grams of powdered sodium chloride, and allowed to remain for 24 hours in the cold. The precipitate is then collected and washed with a saturated solution of sodic chloride. The filtrate is treated with ammonia and allowed to stand for 12 hours. The morphine which crystallises out is separated by decantation, collected on a filter, and washed with as small a quantity of distilled water as possible; it is then dried in a porcelain basin, and treated with an equal weight of a mixture consisting of equal weights of acetic acid (20·4 per cent.) and water. After adding water, the liquid is filtered. The filtrate should not exceed 70—80 grams. An excess of ammonia is added to it, and it is allowed to remain for 12 hours, when the precipitate is collected and weighed. The weight should exceed 1 gram.

*E. Merk's method* is as follows:—15 grams of opium are cut up and boiled with 100 grams of 45 per cent. alcohol. The extract is separated from the residue by filtration, and the latter is again treated with 100 grams of alcohol; 8 grams of crystallised soda are added to

the solution, and it is evaporated without stirring. The residue is treated with 60 grams of cold water, and decanted into a glass cylinder; the clear liquid is poured off, and the undissolved portion washed again with 30 grams of cold water, and then with 45 grams of alcohol (90 per cent.), and finally collected. The crystalline mass remaining on the filter is dried between filter-paper, dissolved in 15 grams of acetic acid (1 part of acid sp. gr. 1.06 to 8 parts of water) and 15 grams of distilled water, and then filtered through the same paper on which the residue was collected. The filtrate is treated with ammonia, and the precipitate is collected and weighed after standing for 12 hours.

The author has devised the following method:—10 to 20 grams of the opium to be examined are boiled for a short time with 15 to 30 grams of caustic baryta and about 150 to 200 c.c. water. The mixture is then filtered, and the residue repeatedly boiled with small quantities of water until the solution fails to give a reaction with molybdic acid and sulphuric acid. Excessive boiling is to be avoided, and as a rule the filtrate should not amount to more than 400—500 c.c. A stream of carbonic anhydride is passed into this solution, which contains all the morphine, until the liquid is supersaturated, and then the whole is evaporated on a water-bath as quickly as possible. The residue is moistened with absolute alcohol, transferred to an Erlenmeyer's flask, and exhausted with successive quantities of boiling absolute alcohol until a sample evaporated on a watch-glass no longer gives a morphine reaction. This usually requires from 300 to 400 c.c. alcohol. The alcohol is removed by distillation, and the residue left in the flask is allowed to stand for some time with 15 c.c. of ammonia. It is next collected on a tared filter, dried at 40°, and treated repeatedly with chloroform. This is the crude morphine. It should be light-brown to straw-coloured. Crude morphine generally contains substances which can be classed under two heads, namely, (1) those which are insoluble in acetic acid; (2) those which are soluble, but which are reprecipitated by ammonia and potassium ferrocyanide. The author finds that the amount of the impurities is always small, and that the difference between the crude and the pure morphine is principally due to the loss of morphine in the process of purification. The following table gives the percentages of morphine found by employing the various methods. The impure products are marked thus \*.

*Percentage of Morphine.*

Opium.	E. Merk.	Aust. Pharm.	Godeffroy.	v. Perger.
I. ....	—	4.17*	1.63*	9.04
II. ....	5.99	2.04*	0.507*	8.37
III. ....	—	—	5.567	9.1
IV. ....	9.32	0.253*	8.52	11.0
V. ....	1.72	0.3*	1.17*	3.68
VI. ....	13.57	?	8.42	14.75

J. I. W.

**Examination of Sugar-beet and Sugar.** By F. STROHMER and others (*Bied. Centr.*, 1884, 277—279).—For the estimation of sugar in pure aqueous solutions only, Abbe's refractometer is recommended; in the original paper tables are given to assist the necessary calculations.

Kohlrausch reports on a new observation tube for saccharimeters introduced by Schmitt and Hänsch; this novelty tends greatly to the exactitude of the polarisation method. Sostmann makes some remarks on the method described by him (*Abstr.*, 1883, 782), for in the earlier part of the season the old method of estimating the sugar in the juice by the polariscope gives higher results than his own when alcohol is used; but as the season advances the difference between the two methods becomes less and less: this must be due to the removal of non-saccharine matters by ripening, which disturbs the polarisation by the old method.

E. W. P.

**Amount of Fatty Acids in Butter.** By REICHARDT (*Arch. Pharm.* [3], 22, 93—102).—Hehner, Turner, and the author have shown that not more than 88 per cent. of solid fatty acids are contained in butter fat. Vegetable oils and animal fats contain 93·8—95·87 per cent. of solid fatty acids. Fleischmann and Vieth found 85·79—89·73 per cent., but accepted Hehner's maximum of 88 per cent.; Kretschmar, by a slight variation of the method, has obtained 89 and 90 per cent.

Reichert's method (*Arch. Pharm.*, 1879, 163; *Zeitschr. Anal. Chem.*, 1879, 68) of determining the volatile fatty acids affords a much better criterion, since 2·5 grams of butter contain volatile acids equivalent to  $14\cdot0 \pm 0\cdot45$  c.c. of decinormal caustic soda solution, whilst coconut oil requires 3·70 c.c., and lard, &c., less than 1 c.c. The above method has been modified in its details by Meissl (*Arch. Pharm.*, 1879, 215, 531), who gives 13·5 c.c. as the lowest limit, and finds that soft butters contain more volatile acids than do harder butters. This method has been again modified by Munier (*Abstr.*, 1882, 247), who found that much less alkali was required, viz., 9·2 to 12·4 c.c., and that the amount, moreover, varies with the season. Ambuhl has obtained numbers confirming Meissl and Reichert's results. In a series of 43 experiments extending from December to the end of October, it is shown that no such variation either in the amount of solid acids or of fatty acids occurs, the numbers obtained being 87·0 to 88·0, mean 87·6, and 13·8 to 14·7, mean 14·16; the animals during this time received very various fodder, and hence the conclusion that neither season nor feeding perceptibly influences the ratio of solid fatty acids to volatile acids. Recent experiments by Birnbaum, and other numerous determinations, have confirmed the numbers given by Reichert and Hehner; Munier's results are not confirmed.

H. B.

**Researches on Milk and Milk-analysis.** By H. VOGEL and others (*Bied. Centr.*, 1884, 273—276).—Vogel recommends the use of the Müller-Soxhlet lactodensimeter when estimating the specific gravity. The dry matter and fat should be estimated by weighing in iron boats half filled with sand, and enclosed in closed glass

cylinders fitted with stoppers; after evaporation the boats should be again weighed in the cylinders; when the fat is to be determined, it is extracted by ether from the sand, &c., wrapped up in filter-paper; the results thus obtained coincide well with those obtained by using Soxhlet's areometer. In legal cases, the lactodensimeter graduated to  $29^{\circ}$  is recommended; in cases of watering and creaming the Feser lactoscope is useful. G. Dangers recounts the police regulations in Celle; amongst them we find that the sp. gr. at  $15^{\circ}$  must lie between 1.029 and 1.033, and the fat must not be less than 2.8 per cent.; the sp. gr. of skim-milk must exceed 1.033; milk under 1.027 is to be considered as watered. Wolff finds Liebermann's method (*Zeitschr. Anal. Chem.*, 1883, 383) unsatisfactory, and amends it by adding to the 50 c.c. of milk 3 c.c. potash solution, 54 c.c. ether, and then evaporating 20 c.c. of the ethereal solution of the fat. Small additions of water are frequently detected by Uppelmann by testing for nitrates, &c., which may be in the bad water added. He proceeds thus: the casein in 350 c.c. milk is precipitated by acetic acid, 100 c.c. of the clear filtrate are then boiled with 3 drops of hydrochloric acid, cooled, and filtered. Of this filtrate 50 c.c. are employed for estimating ammonia by distillation and Nessler's reagent; whilst in the remainder nitrates and nitrites are to be detected by diamidobenzene, zinc iodide, starch, and diphenylamine.

E. W. P.

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## Technical Chemistry.

**Action of Different Antiseptics.** By MIQUEL (*Bied. Centr.*, 1884, 287).—The following table shows the amount of the compound which was required to preserve 1000 c.c. of beef tea:—

	Grams.		Grams.
Mercurous iodide..	0·025	Essence of bitter almonds	3·20
Silver „ ..	0·03	Phenol.....	3·20
Hydrogen peroxide	0·05	Potas. permanganate....	3·50
Mercuric chloride .	0·07	Aniline .....	4·00
Silver nitrate ....	0·08	Alum .....	4·50
Osmic acid .....	0·15	Tannin.....	4·80
Chromic acid ....	0·20	Arsenious acid .....	6·00
Iodine .....	0·25	Boracic „ .....	7·50
Chlorine (gaseous)	0·25	Chloral hydrate.....	9·00
Hydrocyanic acid .	0·40	Ferrous sulphate.....	11·00
Bromine .....	0·60	Amyl alcohol .....	14·00
Chloroform .....	0·80	Ethyl sulphide.....	22·00
Copper sulphate ..	0·90	Borax .....	70·00
Salicylic acid ....	1·00	Ethyl alcohol .....	95·00
Benzoic „ ....	1·10	Potas. thiocyanate ....	120·00
Potas. chromate ..	1·30	Potas. iodide .....	140·00
Picric acid .....	1·30	Potas. cyanide.....	185·00
Lead chloride ....	2·10	Sodium thiosulphate ....	275·00
Mineral acids ....	2·00—3·00		

E. W. P.

**Iodine Extraction.** (*Dingl. polyt. J.*, **253**, 48.)—The process formerly employed in Antofagasta of treating the Caliche mother-liquors with sodium hydrogen sulphite did not extract more than 70 per cent. of the iodine present (*Dingl. polyt. J.*, **231**, 375). Loire and Weissflog first reduce the sodium iodate with calcium sulphide, and precipitate the sodium iodide with copper sulphate and sodium sulphite. The calcium sulphide is produced by igniting calcium sulphate with coal in a rotating furnace. After complete reduction of the iodate, copper sulphate and sodium sulphite are added:— $2\text{NaI} + 2\text{CuSO}_4 + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} = \text{Cu}_2\text{I}_2 + 2\text{NaSO}_4 + \text{Na}_2\text{SO}_4$ . The precipitated cuprous iodide is washed and dried. J. T.

**Purification of Gas Liquor.** (*Dingl. polyt. J.*, **252**, 411.)—Kunheim and Co. propose to remove the ammonium sulphide contained in gas liquor by allowing a powerful and finely divided current of air to act on the crude gas liquor, the ammonium sulphide being split up into hydrogen sulphide and ammonia. The former is passed through finely divided ferric hydroxide suspended in a dilute solution of alkaline earths. D. B.

**Working up Gas Liquor and Gas Purification Residues.** (*Dingl. polyt. J.*, **252**, 476—479.)—In order to obtain the whole of the ammonia contained in gas liquor as ammonium carbonate, Seidler distils the liquor with addition of limestone, dolomite, or similar carbonates. The non-volatile ammonium salts are decomposed thus:  $2\text{NH}_4\text{CNS} + \text{CaCO}_3 = (\text{NH}_4)_2\text{CO}_3 + \text{Ca}(\text{CNS})_2$ . The ammonium carbonate contains a small amount of ammonium sulphide. It is therefore treated in a concentrated aqueous solution with carbonic anhydride, the precipitated ammonium bicarbonate being separated from the mother-liquor and converted into ordinary ammonium carbonate by sublimation. The carbonic anhydride given off during the sublimation is passed into fresh portions of ammonium carbonate solution, whilst the mother-liquor is treated with sulphuric acid and worked up into ammonium sulphate.

For the recovery of ferrocyanides from gas purification residues, Kunheim and Zimmermann desulphurise the liquors in the usual manner, and remove the soluble ammonium salts by washing with water. The product is then mixed intimately with caustic lime and heated in closed agitators at 40—100°. Thus the fixed ammonia salts are decomposed, their ammonia being passed into sulphuric acid, whilst a solution of calcium ferrocyanide is obtained. The latter is converted into ferric ferrocyanide (Prussian blue) by precipitation with a proto-salt of iron and subsequent oxidation. If it be desired to obtain potassium ferrocyanide from the liquors, potassium and calcium ferrocyanide is first prepared by evaporating the liquors and adding the quantity of potassium chloride necessary to form the double salt: on boiling the latter with a solution of potassium carbonate, it is converted into potassium ferrocyanide. The advantage of this process is the saving of potassium carbonate, only half the requisite quantity being used, the remaining half being supplied by potassium chloride, a less valuable salt of potassium. D. B.

**Loss of Nitre in the Manufacture of Sulphuric Acid.** By G. ESCHHELLMANN (*Dingl. polyt. J.*, **252**, 431—434).—The loss of nitre in the manufacture of sulphuric acid is of two kinds, first mechanical loss, such as nitrous acid kept in solution by sulphuric acid, nitrous acid escaping unabsorbed at the Gay-Lussac tower and through leakage of the chambers; secondly, chemical loss through reduction of nitrous gases to nitrous oxide and nitrogen. To trace out these losses, the author has made a series of experiments on the chambers in Muspratt's works at Widnes. The mechanical loss at the Glover tower is in the acid used for the manufacture of salt-cake; this, as well as the loss through leakage of the chambers, is very slight. The Glover acid, by analysis, showed only traces of nitrous anhydride. The mechanical loss by non-absorption at the Gay-Lussac tower was determined by drawing the gases with a water-pump through concentrated sulphuric acid, then through caustic soda, and finally through potassium permanganate, to absorb nitric oxide. The sulphuric acid was tested in the nitrometer, the permanganate was reduced with a solution of a proto-salt of iron, then boiled with a known weight of iron solution, and titrated back with permanganate. Simultaneously, a second test was taken by means of an aspirator, the gases not absorbed by caustic soda being tested for oxygen. These analyses were performed daily, the following table giving average results for several quarters:—

	Cubic metres of chamber space per kilo. S.	Nitre used per cent. on S.	Oxygen at outlet per cent.	Unabsorbed nitric oxides soluble in $\text{H}_2\text{SO}_4$ per cent. total loss of $\text{NaNO}_3$ .
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*First System.*

Quarter I ..	1·34	3·24	6·0	10·70
Quarter II ..	1·47	2·75	7·0	11·50

*Second System.*

Quarter I ..	1·34	3·24	6·1	12·02
Quarter II ..	1·47	2·75	7·0	12·50

The Gay-Lussac towers belonging to these systems represented 1·6 per cent. of the total chamber space, the strength of the nitrous liquors being 1 per cent.  $\text{N}_2\text{O}_5$ . The loss through escape of nitric oxide at the Gay-Lussac tower amounted to 7 per cent. of the total. The mechanical loss is represented by the following percentages:—

1. Glover acid, traces (below 1 per cent.)
2. Gay-Lussac tower } as  $\text{N}_2\text{O}_5$  12 per cent.  
19 per cent. } as  $\text{NO}$  7    "
3. Leakage, &c..... 2    "



From the results obtained by Lunge and Naef, the author infers that the best way to avoid loss of nitre is to have all gases leaving the system of chambers in the form of nitrous anhydride, and to prevent the presence of nitric oxide or tetroxide in the gases. The author further shows that an increase of steam by one-third raises the temperature by  $2.6^{\circ}$ , the variation of temperature caused by variation of steam is therefore very slight, and depends mainly on the energy of the chemical reaction, that is, on the quantity of sulphuric acid formed. Experiments were made with two systems of chambers. The first system received a continuous supply of nitrous liquors, and therefore showed no variation of temperature, whilst the second system was fed with periodical supplies at intervals of two hours, the temperature varying between  $48^{\circ}$  and  $68^{\circ}$ , this variation repeating itself regularly after each addition. It appears to be more advantageous, therefore, to have a continuous supply of nitrous gas entering the chamber.

Lunge has shown that on mixing sulphurous anhydride, air, water, and nitric oxide, considerable quantities of nitrous oxide are formed. These conditions are fulfilled in the chambers at the inlet of the steam. It being impossible to analytically determine nitrous oxide, the author tried to find out whether, in the manufacture of very weak acid ( $114^{\circ}$  Tw. =  $\text{SO}_3 + 4\text{H}_2\text{O}$  instead of  $3\text{H}_2\text{O}$ ) an increase in the loss of nitre through increased reduction took place in the first chamber. The temperature, perfectly constant under ordinary conditions, rose at once  $3^{\circ}$ , after which it began to fall to  $46^{\circ}$ , which fall took 48 hours, so that nitre had to be introduced, the same fall of temperature repeating itself. During the 96 hours the experiment lasted, the extra nitre used weighed 30 kilos., representing  $10\frac{1}{2}$  per cent. of the total loss of nitre (2.76 per cent.). This is the loss through reduction in the production of  $\text{SO}_3 + 4\text{H}_2\text{O}$  instead of  $\text{SO}_3 + 3\text{H}_2\text{O}$ . Assuming that the same amount is reduced for the first three equivalents of water, 31.5 per cent. of the total nitre is lost through reduction.

In conclusion, it is stated that there has always been much difference of opinion as to the amount of oxygen in the chamber exit gases. According to the author, it depends greatly on the available chamber space, the following table giving the results of working chambers with different spaces:—

Chamber space, cubic metres per kilo. S.	Oxygen per cent. per vol.	Loss of nitre per cent. on sulphur.
1.0	4.5—5.0	4.0
1.1	5.0—5.5	3.7
1.2	5.5—6.0	3.5
1.3	6.0—6.5	3.1
1.4	6.5—7.0	2.8

Working the chambers much higher in oxygen increases the loss of sulphurous anhydride considerably, whilst when the oxygen is reduced, a greater quantity of extra nitre has to be used. The total loss of nitre (2.75 per cent.) may be apportioned as follows:—

	Percentage on S.	Percentage of total loss.
Gay-Lussac tower ..	0.330 p. c. =	12 p. c. as nitrous gases soluble
" " " ..	0.192 " =	7 " as NO. [in H <sub>2</sub> SO <sub>4</sub> .
Glover tower, leakage, &c. ....	0.082 " =	3.0 "
	0.866 " =	31.5 " reduced by the steam.
	<hr/> 1.470 " =	53.5 " accounted for.
	1.280 " =	46.5 " unaccounted for.

D. B.

**Strontium Hydroxide.** (*Dingl. polyt. J.*, **253**, 82—84.)—C. F. Claus proposes to obtain strontium hydroxide from the chloride by the addition of an equivalent of barium hydroxide to the hot solution. Strontium hydroxide crystallises out, and barium chloride is obtained by evaporation and crystallisation. Similarly, Claus prepares strontium hydroxide from the sulphide or sulphhydrate by adding to the hot sulphide solution an equivalent of barium hydroxide. Further, if to a hot solution of strontium sulphide a solution of barium sulphide be added in equivalent quantity, strontium hydroxide is formed, and crystallises out on cooling, whilst barium sulphhydrate remains in solution. It is advisable to employ an excess of strontium compound to avoid contamination of the product with baryta. On mixing hot solutions of sodium sulphide and strontium sulphide, a similar reaction takes place. By evaporating solutions of barium sulphhydrate and sodium sulphhydrate, mixing with coal-dust, igniting gently, and lixiviating, solutions of barium sulphide and sodium sulphide, respectively, are obtained, which can be again employed. Mother-liquors containing strontium sulphhydrate, when evaporated and ignited with coal-dust, give strontium hydroxide on lixiviation with hot water. The mother-liquor, after the separation of the crystals, consists of strontium sulphhydrate, and is treated in a similar manner until all the strontium is obtained as hydroxide. If the solution of strontium sulphhydrate is treated with an equivalent of sodium sulphate, a precipitate of strontium sulphate is formed, which can be filtered off, mixed with coal-dust, and ignited like fresh celestine. The ignited mass, when extracted with water, gives strontium hydroxide. Strontium sulphhydrate can also be decomposed by magnesium sulphate. Strontium carbonate is obtained from a solution of the sulphhydrate by adding an equivalent of magnesium chloride, boiling to expel hydrogen sulphide, and then passing into the solution carbonic anhydride, by which strontium carbonate is precipitated and magnesium chloride is reformed. Hot furnace gases, deprived of free oxygen, can be used for this purpose.

To obtain zinc sulphide and strontium hydroxide, Claus treats calamine with ammonia solution, precipitates zinc sulphide by means of potassium sulphide, and distils off the ammonia from the solution. The potassium carbonate remaining in solution is rendered caustic by means of lime, and treated with a hot solution of strontium sulphide. On cooling, strontium hydroxide falls out, and the potassium sulphide can be used over again to precipitate fresh zinc solution.

J. T.

**Process for Working up Strontium Sulphate.** (*Dingl. polyt. J.*, 252, 332.)—Urquhart and Rowell treat native strontium sulphate (cœlestine) with sulphuric acid to remove the greater portion of the iron and alumina. The product is then boiled with a mixed solution of sodium sulphate and sodium carbonate. The resulting mixture of strontium sulphate and carbonate is heated in a furnace with an excess of sodium carbonate, and on lixiviating the melt with hot water strontium carbonate is obtained, together with the liquor used for the first treatment of the strontium sulphate. D. B.

**Cement and its Adulteration.** (*Dingl. polyt. J.*, 253, 426—431.)—This paper is an abstract from the report of the general meeting of the German Society of Cement Manufacturers, held in February 1884. The question in regard to the adulteration of Portland cement with less valuable substances was again discussed. Böhme stated that in his experiments on the influence of additions to mixed

Name.	I. Sp. gr.	II. Loss on ignition.	III. Alkalinity of the water in which 0·5 gram of the sub- stance is placed, Decinormal acid used.	IV. 1 gram of sub- stance requires normal acid.	V. 1 gram of sub- stance reduces potassium permanga- nate.	VI. 3 grams of sub- stance absorb carbonic anhydride.
Portland cements—		p.c.	c.c.	c.c.	mg.	mg.
A.....	3·155	1·58	6·25	20·71	0·79	1·4
B.....	3·125	2·59	4·62	21·50	2·38	1·6
C.....	3·155	2·11	4·50	20·28	0·93	1·8
D.....	3·144	1·98	5·10	21·67	1·12	1·0
E.....	3·144	1·25	6·12	19·60	0·98	1·6
F.....	3·134	2·04	4·95	20·72	1·21	1·1
G.....	3·144	0·71	4·30	20·20	0·89	0·0
H.....	3·125	1·11	4·29	20·30	1·07	0·7
I.....	3·134	1·00	4·00	19·40	2·01	0·0
K.....	3·144	0·34	4·21	20·70	0·98	0·0
L.....	3·154	1·49	4·60	18·80	2·80	0·3
M.....	3·125	1·25	5·50	20·70	2·33	0·0
Hydraulic limes:—						
A.....	2·441	18·26	20·23	21·35	1·40	27·8
B.....	2·551	17·82	22·73	26·80	0·93	31·3
C.....	2·520	19·60	19·72	19·96	0·98	47·7
Slag dusts:—						
A.....	3·012	0·76	0·91	14·19	74·67	3·6
B.....	3·003	1·92	0·70	13·67	60·67	3·5
C.....	2·967	1·11	1·00	9·70	44·34	2·9
Ground slags:—						
A.....	3·003	0·32	0·31	3·60	64·40	2·4
B.....	2·873	0·43	0·11	8·20	73·27	2·2

cements, he never experienced an increase in the tenacity as against that of unadulterated cement; moreover, the bearing qualities of mixed cements are less than those of unmixed cement. Dyckerhoff experimented in a similar direction. His results, which are tabulated in the original paper, clearly demonstrate the injurious effect of additions on the tenacity and durability of Portland cement.

Fresenius has undertaken a series of experiments on Portland cement at the request of the above Society. He obtained twelve samples of pure cement from different parts of Germany, England, and France, and these were compared with three kinds of hydraulic lime, three of weathered slag-dust, and two of ground slag. The results are illustrated by the table, p. 1225.

The numbers in the case of pure Portland cement should be as follows:—(1), sp. gr. at least 3.125, not lower than 3.1; (2), loss on ignition between 0.34 and 2.59 per cent., or at least not much higher; (3), alkalinity of aqueous solution of 0.5 gram of cement, corresponding to 4 to 6.25 c.c. of decinormal acid; (4), volume of normal acid neutralised by 1 gram of the cement 18.80 to 21.67 c.c.; (5), weight of potassium permanganate reduced by 1 gram of cement between 0.79 and 2.80 mgrms., or at least not much higher; (6), weight of carbonic anhydride absorbed by 3 grams of cement 0 to 1.8 mgrms. The tests, I, III, IV, and V, are applicable for the detection of slag, and I, II, III, and VI, for the detection of hydraulic lime. Experiments were made by mixing 9 parts of pure Portland cement with 1 part of hydraulic lime, with 1 part of slag-dust, and with 1 part of ground slag respectively, and it was found that the adulteration could in every case be detected by the determinations given above.

D. B.

**Process for the Recovery of Slag.** (*Dingl. polyt. J.*, 252, 528.)—Frank (Ger. Pat. 27,106, September, 1883) utilises a solution of magnesium chloride of 1.06 sp. gr. for dissolving sulphuretted and phosphoretted slags. The fluid mass is poured into this solution, the sulphides and sulphites contained in the slag being decomposed; whilst the combined lime present in the basic slag is converted into calcium chloride, and thus indirectly effects a concentration and facilitates the solution of the phosphates contained in the slag.

D. B.

**Formation and Employment of Slags.** (*Dingl. polyt. J.*, 253, 163—173; 204—206.)—G. Hilgenstock finds that no phosphorus is carried away by the waste gases of the blast furnaces. The phosphorus is usually introduced as iron or calcium phosphate, and as the presence of iron induces the reduction even of earthy phosphates by carbon, it may be accepted that the whole of the reduced phosphorus is reduced only on account of its great affinity for iron, and forms iron phosphide.

Finkener has shown (*ibid.*, 249, 264) that tribasic iron phosphate, heated in a stream of hydrogen, first gives steam at a clear red heat, and at a white heat hydrogen phosphide and phosphorus are produced; but the reaction is not very probable in a blast furnace where the hydrogen from the moisture introduced by the blast is so dilute, and the amount of phosphate is so small. The less reducing agent is

present, and the lower the temperature, the more phosphoric acid goes into the slag. The analyses of 23 successive runnings of highly phosphoric pig show the following limits:—

P....	3.26 per cent.	Si....	1.03	C....	2.01
„....	12.12 „	„....	0.02	„....	0.87

so that, other things being equal, silicon and carbon diminish as phosphorus increases. Carbonic oxide, at high temperatures, is more stable than silica or phosphoric acid, and silica is more stable than phosphoric acid. It is not the phosphorus as such which replaces the carbon and silicon, but the phosphoric acid, at whose expense silicon and carbon are oxidised. If the oxygen of the phosphoric acid be not present, that is, if an iron rich in phosphorus be fused with one rich in silicon or in carbon, the whole amount of the three elements is found in the alloy. Iron rich in phosphorus, with 0.8 per cent. carbon and no silicon, is exceedingly fluid when fused. The amount of phosphorus that may be retained by iron appears to be unlimited, as in the case of manganese. One sample contained 25.65 per cent. The iron becomes more and more brittle, and the fracture crystalline, similar to that of ferromanganese. Such iron also becomes less and less affected by the magnet. Iron with 9.6 per cent. phosphorus is sensibly less magnetic than ordinary iron. With 16 per cent., a powerful magnet had only slight action, whilst with 25.6 per cent. the action was scarcely perceptible.

A. Ledebur considers fluid slags as solutions of various oxygen compounds in one another, whose constituents can arrange themselves in various groups during cooling. Analyses are given of slags which had been slowly and rapidly cooled; but the differences in composition are too slight to account for physical differences. It is noticeable that slag cooled quickly is rapidly and almost completely decomposed by hydrochloric acid, whilst that cooled slowly resists the action of the acid very strongly.

The richer a pig iron is in carbon, silicon, and manganese, and the higher the furnace temperature is, so much the less iron goes into the slag. The lower the temperature, the more manganese goes into the slag. If the temperature be higher and the fuel applied be more than is required to reduce all the manganese in the charge, then silicon is reduced. Grey pig is formed when the amount of manganese present is not sufficient to prevent the formation of graphite induced by the silicon, or in presence of much manganese a silicon-iron-manganese alloy is formed. Owing to the higher temperature in the Bessemer process, the affinity of carbon for oxygen is considerably increased as compared with the puddling process. As long as carbon is present in the bath, the amount of iron in the slag will be less than in puddling furnace slag. When the carbon has disappeared, the slag is still poorer in iron, owing to the action of the iron in the slag on the converter lining. The higher the temperature and the richer the iron is in manganese, the less iron goes into the slag. Continued blowing after the carbon has been removed increases the proportion of iron in the slag; but if, on the other hand, the burning of certain substances, as phosphorus in the basic process, increases the

final temperature, and also increases the amount of slag, the proportion of iron is diminished thereby.

In the Siemens-Martin process, the temperature is high and the furnace lining is siliceous, so that the slag must contain considerably more silica and less iron than in the older refining processes for producing wrought iron. On the whole, the slags range between the same limits as Bessemer slags do. A detailed account is given of the working of two baths in this process. The silica in the slag always increases with the manganese, and with the temperature at which the charge has been worked, whilst the amount of iron falls as the temperature has been higher, and as the manganese and carbon of the iron have been higher.

L. Garnier has applied blast furnace slag as a preventive of phylloxera in vineyards with advantage: this is attributed to the sulphur present in the slag.

R. Hasenclever describes Scheibler's method of treating basic slags (this vol., p. 783). The slag is roasted, treated with steam, and free lime removed as milk of lime by washing with water. The residue is then treated with hydrochloric acid in suitable quantity, about 1.25 to 1.5 kilos. of acid to 1 kilo. of slag. The solution separated from the insoluble residue is now precipitated by means of the milk of lime previously obtained. The dicalcium phosphate can be directly applied for agricultural purposes. The calcium phosphate can easily be obtained containing 35—37 per cent. of phosphoric acid.

*Potassium Ferrate and Manganate.*—B. Platz found a deposit in a blown-out blast furnace, reaching down to the boshes, about 0.6 m. thick, consisting of a slaggy mass of grey to black colour. In water it gave a deep-red solution of potassium ferrate. Minute black needle-shaped crystals were visible in the cavities of the mass; also a bluish-green crust of potassium manganate covered some of the fragments. Two samples of the deposit had the following composition:—

Fe <sub>2</sub> O <sub>3</sub> .....	13.72	7.83
FeO .....	24.75	12.77
MnO.....	0.46	0.92
SiO <sub>2</sub> .....	11.98	6.66
Al <sub>2</sub> O <sub>3</sub> .....	6.72	3.10
CaO .....	33.02	59.62
MgO.....	1.27	1.41
CaS .....	1.35	1.37
	<hr/>	<hr/>
	93.27	93.66

The remainder was mainly alkaline carbonates and sulphates.

J. T.

**Utilisation of Metallic Slags rich in Phosphorus.** (*Dingl. polyt. J.*, **253**, 135—136.)—Rocour, in a supplementary patent, modifies his plan for treating such slags. By a reducing fusion in a blast furnace, a regulus is obtained containing 20—20.5 per cent. phosphorus. The powdered regulus is mixed with finely-divided anhy-

drous sodium sulphate, say 3—7 parts to each part of phosphorus in the regulus, and the mixture is heated to redness in a flame as little oxidising as possible; a large portion of the phosphorus becomes converted into sodium phosphate with development of heat; whilst a portion of the iron and manganese becomes converted into phosphate, sulphide, and oxide. The mass, when treated with water, gives a solution of sodium phosphate. If the insoluble residue contains a considerable amount of iron and manganese phosphate, it is dried, powdered, and heated with sodium sulphate and coal-dust. On heating the mixture to redness in a reducing flame, the sulphate becomes sulphide, and, at a high temperature, sodium phosphate is formed, the iron and manganese becoming converted into sulphide. After washing out the soluble sodium phosphate, the residue can be roasted free from sulphur, and may be used as a manganiferous iron ore. The procedure is rapid, but the reactions are not very complete, so that a considerable amount of phosphorus remains insoluble. Instead of sodium sulphate, soda or potash may be used; also nitrates of these bases. The phosphorus regulus can also be blown in a basic-lined converter, with gradual addition of lime or dolomite. A basic slag, relatively poor in iron and manganese, is obtained, which is sufficiently rich to serve as manure, or may be used for the production of superphosphate. The metals may be converted into steel in the same heat. J. T.

**Earthenware Enamels.** (*Dingl. polyt. J.*, 252, 374—379.)—Heinecke gives an account of experiments made with different glazes, from which the following conclusions may be drawn: Alumina glass, composed of several flux radicles, is more transparent than glass of a similar character, but containing less flux radicles. Glaze composed of materials which yield glass with great difficulty, should contain a larger proportion of silicic acid than glaze formed from more readily fusible substances, to prevent their decomposition by the action of the clay mass at an elevated temperature, or of the atmosphere at the ordinary temperature. A certain amount of boric acid prevents the devitrification of the glaze by the bases of the clay substance. Acid alumina enamels are less subject to devitrification than enamels containing a smaller amount of acid and alumina. Calcareous enamels do not adhere firmly to clay masses, when they contain a large percentage of lime, such as the Velten clay masses.

Schumacher attributes the cause of the severance of the enamel from the clay substance to a tension between them, occasioned mainly by the presence of a large amount of silicic acid.

Seger discusses, at some length, the influence of sulphuric acid on glazes. The formation of blisters on porcelain is due to the presence of sulphuric acid, or sulphates in the composition of the enamel, or in the water employed for making it up. D. B.

**Extraction of Metals by Electricity.** (*Dingl. polyt. J.*, 253, 32—33.)—R. P. Hermann treats zinc ores with acids, and precipitates the metal electrolytically, after converting it into a double alkaline, or alkaline earthy salt.

M. Kiliani proposes to extract calamine, zinc-ash, &c., with ammoniacal liquor containing carbonate, and then to precipitate electrolytically, employing iron anodes.

M. Body recommends mixing the powdered ore with ferric salts alone, or with the addition of common salt, by which advantage is taken of the property of ferric salts to pass into the ferrous state in the presence of metallic oxides or sulphides, under the influence of an electric current. This change leads to the solution and precipitation of the metal, subsequently the ferrous salt can be readily converted into the ferric state, and is again ready for use. The finely powdered mineral is exposed, in moist heaps, to the action of the air, and repeatedly ground. The ore may then be placed in a tank provided with a bottom of pressed coke, in which is embedded the negative pole of a dynamo, whilst the other pole is connected with the ore at one or more points.

In treating certain ores of gold and silver, a cast-iron drum is employed, which is connected with the negative pole of a dynamo, and is slowly revolved. Within the drum are several cast-iron balls. Through the drum, and isolated from it, passes a fixed axle, which is connected with the positive pole of the machine, and which carries a series of coke or graphite plates dipping into a solution of ferric salts containing the mineral. The axle is hollow, and serves for the introduction of liquid to the drum; a steam pipe, terminating within the liquid, also passes through it. When the silver is reduced, mercury is passed into the drum, and the amalgam is collected in the ordinary way. The method is advantageous for ores which contain only 0.05 per cent. of silver.

J. T.

**Improvements in Metallurgy.** (*Dingl. polyt. J.*, 252, 515—519.)

—For the preparation of aluminium, and alloys of aluminium, Weldon fuses cryolite with calcium chloride, or other non-metallic chloride, or sulphide, and reduces the resulting aluminium chloride, or sulphide, with manganese, to which sodium may be added.

Frishmuth proposes to heat ignited bauxite, or corundum, in retorts, to the temperature of volatilisation. The ascending fumes of alumina are brought into contact with the vapour of sodium, the resulting aluminium being obtained in the form of a fine dust, which is made into balls by fusion with fluxes.

Niewerth mixes ferrosilicon with aluminium fluoride in equivalent proportions, and fuses the mixture, the products being volatile silicon fluoride and an alloy of iron and aluminium. In order to prepare aluminium-bronze therefrom, the alloy is fused with copper. By substituting aluminium chloride for the pure aluminium fluoride, silicon chloride and an alloy of aluminium and iron are said to be formed; pure silicon is said to yield pure aluminium with aluminium chloride.

To extract metals from certain ores, burnt pyrites, slag, &c., Föhr employs a weak solution of magnesium, calcium, or sodium chloride, with or without the application of heat. The main portion of copper, lead, and similar metals, are dissolved. The lixiviated ore is then treated with bromine-water in the dark, which dissolves the gold



completely and the silver partially, all metallic sulphides of copper, lead, zinc, &c., being decomposed. Finally the ore is again treated with the above chloride liquor, when the silver and lead are completely removed.

Lipp and Schneider give the following analyses of iron: I, charcoal pig iron from Hieflau in Styria; II, grey pig iron from Witkowitz in Moravia; III, the same from Rokycan in Bohemia; IV, grey pig iron; V, steel; VI, steel plate, all three from Neuberg in Styria; and VII, "Kudsilver Normalstahl."

	I.	II.	III.	IV.	V.	VI.	VII.
Carbon combined.	2.442	0.370	0.125	0.257	0.164	0.131	0.873
Graphite .....	1.631	3.414	2.830	3.425	—	—	—
Silicon .....	0.684	3.640	3.951	1.353	0.023	0.014	0.280
Phosphorus .....	0.068	0.701	1.412	0.059	0.067	0.030	0.021
Sulphur .....	0.025	0.015	0.044	0.001	0.011	0.026	0.011
Copper .....	trace	0.252	trace	0.029	0.060	0.163	0.044
Cobalt and nickel.	trace	0.030	0.025	0.019	0.008	0.030	trace
Manganese .....	2.992	1.834	0.169	3.414	0.088	0.180	0.215
Iron by difference	92.158	89.744	91.444	91.433	99.579	99.426	98.556

Flue dust from Neuberg contained, according to Schneider, when dried at 100°—

Fe <sub>2</sub> O <sub>3</sub> .	FeO.	Mn <sub>2</sub> O <sub>4</sub> .	CuO.	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.
40.50	16.59	2.98	0.06	2.95	6.35	3.93
K <sub>2</sub> O and Na <sub>2</sub> O.	SiO <sub>2</sub> .	SO <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	C.	CO <sub>2</sub> and H <sub>2</sub> O.	
0.85	13.75	0.30	0.072	4.75	6.79	

Zinc from Sagor, in Carniola, contained 0.943 per cent. lead, 0.008 iron, and 0.002 sulphur. According to Lipp and Schneider, tungsten steel (I), and tungsten iron (II), had the following composition:—

Fe.	W.	Mn.	Co and Ni.	Si.	P.	S.	C.
I. 85.0	11.028	1.493	traces	0.263	0.007	trace	2.147
II. 68.363	28.181	0.986	trace	0.233	0.008	trace	1.882

The method adopted by Lipp and Schneider for conducting these analyses is briefly described in the original paper. D. B.

**Preparation of Magnesium.** By J. WALTER (*Dingl. polyt. J.*, **252**, 337—339).—The author has made a series of experiments in order to determine whether Marquardt's suggestion to prepare magnesium by distilling magnesia with coal in zinc furnaces is practicable. According to the views upheld by Weldon, this reduction would be impossible, as in this case the same thermochemical relations which stand for aluminium are applicable. By the combustion of magnesium 74,900 cal. are liberated, according to the equation  $\text{Mg} + \text{O} = \text{MgO}$ .

The reduction would be effected in accordance with the equation  $2\text{MgO} + \text{C} = 2\text{Mg} + \text{CO}_2$ , which requires  $2 \times 74,900 = 149,800$  cal. (whilst the heat of formation of carbonic anhydride only amounts to 97,000 cal.), or according to the equation  $\text{MgO} + \text{C} = \text{Mg} + \text{CO}$ , which requires 74,900 cal., the combination of  $\text{C} + \text{O} = \text{CO}$ , yielding only 29,000 cal. These numbers do not however correspond with the conclusion drawn therefrom, viz., that the reduction of an oxide only takes place when the heat of combination of the element with oxygen is less than that of the reducing agent with oxygen. Weldon explains this contradiction by supposing that, in the case of aluminium, the reduction of sodium from its carbonate, by means of carbon, depends on a preliminary process of dissociation. Fischer, on the other hand, shows that the decomposition of steam by carbon occurs at  $300\text{--}350^\circ$ , a temperature at which steam could not undergo dissociation.

In order to obtain the requisite temperatures, the author made use of Perrot's gas furnace. In the first series of trials, the temperature employed was a bright red heat, magnesium in the form of oxide, carbonate, and tartrate, being used, whilst in the second series of experiments, the same materials were exposed to an extreme white heat. Although the conditions were more favourable than in the case of zinc furnaces, the author failed to obtain reduced magnesium.

D. B.

**White Lead Manufacture.** (*Dingl. polyt. J.*, 252, 372—374.)—Roth and Sylvester propose to pass an electric current through a solution of sodium acetate, using lead plates as poles. Lead acetate is said to be formed at the positive pole, whilst free sodium hydroxide is produced at the negative pole, the mixture of the two resulting in the precipitation of lead hydroxide, which is converted into white lead by the introduction of carbonic anhydride.

Gardner recommends to heat lead with graphite, carbon, platinum, or similar substances (all of which should be electronegative to lead) in a solution consisting of 1 part lead acetate, or 1 part nitric acid, in 40 parts water, or acetic acid in 24 parts water. Basic lead salts, or lead oxide, or lead suboxide, is said to be produced. After the lapse of one to two hours, the lead is taken out of the solution, and the latter on addition of acetic acid, or nitric acid, used for a further operation. If the conversion of the lead is effected in chambers, the metal is brought into contact with carbon or platinum, according to various modes of arrangement. Ozonised air is introduced into the chamber, or produced therein by electric discharges.

D. B.

**Manufacture of Cuprammonium and Zincammonium Compounds, and their Technical Application.** By C. R. A. WRIGHT (*Dingl. polyt. J.*, 253, 37—38, from *Jour. Soc. Chem. Industry*, 1884, 121).—During the past few years, many attempts have been made to utilize on a manufacturing scale the power possessed by cuprammonium and zincammonium solutions of pectising cellulose and similar substances, so as to produce a kind of vegetable parchment. The process consists essentially in the preparation of a concentrated solution of cuprammonium hydroxide, and the passing of the goods to be treated

through a bath of this material at just such a rate as will permit of the pectising and gelatinising of the exterior of the fibres composing the paper or canvas, &c., without wholly disintegrating the mass; so that the material on emerging from the bath retains coherence enough to enable it to be passed through the usual drying apparatus of a paper-mill. This drying converts the film of pectised cellulose coating each filament into an insoluble solid varnish. In order to build up thick cards, two or more layers of paper are passed simultaneously through the bath, and then pressed together and dried as a whole. By careful treatment, the copper present in the solution taken up by the material is wholly converted during the drying into a compound with the pectised cellulose. Mineral acids dissolve out the copper. Instead of cuprammonium hydroxide alone, in certain cases a mixture of this with zincammonium hydroxide may be used. The pectised cellulose then contains both zinc and copper, indicating apparently that a zinc cellulose compound has also been formed. Zincammonium hydroxide alone, however, does not pectise paper sufficiently to give good results. Cuprammonium salts give less satisfactory results than the hydroxide. The solution employed contains from 100 to 150 grams ammonia and 20 to 25 grams of copper per litre; this is prepared by the action of ammonia solution on copper turnings in the presence of a current of air. Brass turnings give the zinc-copper compound. Zinc alone is only slightly attacked under these conditions. The presence of iron accelerates the solvent action. Pure cuprammonium solution has absolutely no effect on iron.

Experiments made to ascertain the amount of ammonia carried off from an aqueous solution by a current of air showed that in dissolving 11.4 kilos. (25 lbs.) of copper in ammonia solution (150 grams  $\text{NH}_3$  in 1 litre), 2 to 9 kilos. (5 to 20 lbs.) ammonia, according to the temperature, were removed. In practice, this ammonia is recovered in the form of a weak copper solution. The solubility of the copper diminishes gradually as the liquid becomes richer in that metal. Also when the solution is proceeding most rapidly only a small portion of oxygen passed into the solution is absorbed. When the concentration of the copper solution does not exceed 12 to 15 grams per litre, it is very stable; such a solution is well adapted for the preservation of sleepers and timbers generally. J. T.

**Extraction of Cobalt and Manganese from their Ores.** (*Dingl. polyt. J.*, 252, 392.)—Herrenschmidt and Constable treat ores containing cobalt or manganese with ferrous sulphate and enough water to form a paste; the iron salt is said to react on the oxides of cobalt and manganese contained in the ores; on boiling the mixture a solution of cobaltous or manganous sulphate is obtained, which is separated from the residue and treated with a suitable agent, so as to convert the proto-salt into the corresponding per-salt.

D. B.

**Absorption of Carbonic Anhydride by Beer.** By T. LANGER (*Bied. Centr.*, 1884, 286).—The amount of gas which beer will absorb is dependent on the temperature and on the pressure, for at 0—5° with constant pressure the amount present = 0.01 weight per

cent. = 50 c.c. per litre for every 1°; and the same increase is observable when the temperature remains constant, but the pressure increases 31.3 mm. mercury. Strong beer absorbs a larger volume of gas than weak beer, other things being equal. Water mixed with alcohol absorbs less gas than water alone, and the reducing effect of alcohol on absorption increases within limits with the increase of alcohol, and more especially is this remarked at low temperatures; yet, for all this, 1 litre beer can absorb more carbonic anhydride than the same quantity of water at the same temperature.

E. W. P.

**Date-sugar.** (*Bied. Centr.*, 1884, 284.)—Date-sugar is obtained from the palm by making incisions in the lower branches, and collecting the sap which flows nearly continuously from November up to March; the sap is then clarified and boiled down.

E. W. P.

**Manufacture of Starch.** By C. SCHAUB (*Bied. Centr.*, 1884, 285). When the yield of potato-starch is low, it arises from one of three causes—(1) low quality of potatoes; (2) the potatoes, although good, may, by reason of a deficiency of water, not yield up all the starch they contain, and this is frequently the case, especially in small factories; (3) potatoes and supply of water being good, the machinery may work ineffectively. The author mentions additions to the machinery which should be made.

E. W. P.

**Bleaching Yarns and Fabrics.** (*Dingl. polyt. J.*, 252, 392.)—Thomson and Rückman (Ger. Pat., 26,839, March, 1883) boil linen yarns and fabrics for three hours in a solution containing 2.4 grams potassium cyanide in a litre of water, wash, and repeat this treatment. For cotton, this operation may be omitted, unless the material has been brought in contact with fatty or oily substances, in which case the above solution is used in a more dilute form (half the strength). The fabric thus prepared is placed in closed vessels, and treated with a solution of chloride of lime containing 5.3 grams per litre. As soon as the vessel is full, the solution is drawn off, and carbonic anhydride passed in. This operation is repeated until the fabric assumes the desired degree of whiteness. It is then taken out, washed in water, and pressed. In most cases a slight yellow tinge is retained within the fabric, owing to the presence of traces of iron in the bleaching agent. To remove this coloration, the fabric is drawn through a bath of oxalic acid (about 4.6 grams per gallon), washed with water, pressed, and toned with indigo or aniline violet.

D. B.

**Gaseous Chlorine as Discharge in Calico-printing.** By A. SCHEURER (*Dingl. polyt. J.*, 253, 208–211).—In his handbook on calico-printing, J. Persoz has pointed out that indigo-blue can be discharged by gaseous chlorine; chlorine in the dry state attacks indigo slowly, but in the presence of water the action is rapid. Experiments, however, show that the practical application of the proposal is difficult, as the goods must be exposed to the gas for at least two minutes, and in this time the dry blue colour is sensibly affected. The following is a means of reducing the time of exposure required: a piece moistened

with weak soda-lye had its blue colour discharged with only 10 seconds' exposure to chlorine; a lye of about 16—17° B. is most suitable. Turkey-red thus treated became yellow in 20 seconds, and white in 50 seconds. Aniline black is destroyed immediately. A mixture of aniline oil and soda-lye, printed and exposed to chlorine, causes the formation of an intense black compound which contains chlorine, whilst a solution of aniline salt alone under similar conditions gives a lively chamois-yellow of very stable character, which is not destroyed by prolonged exposure to chlorine. If on the contrary a drop of soda-lye be placed on the dye, and it be again exposed to chlorine, the colour is then discharged. Hypochlorites, even when concentrated, do not act rapidly on indigo. Free hypochlorous acid acts like chlorine in the presence of soda. This acid cannot act in the free state in this reaction, since free alkali is present; and in fact after the colour has been discharged by chlorine in the presence of soda, the piece has an alkaline reaction. The active agent is apparently oxygen as hydroxyl,  $2\text{NaHO} + 2\text{Cl} = 2\text{NaCl} + 2\text{HO}$  and  $2\text{HO} = \text{H}_2\text{O} + \text{O}$ . J. T.

**Kephir.** By H. STRUVE (*Ber.*, 17, 1364—1368).—Kephir is a variety of fermented milk prepared in the Caucasus, the use of which for medicinal purposes has in the last two years spread over a great part of Russia. It is prepared from milk by fermentation with the so-called kephir-grains in leather bottles. During the fermentation, a considerable quantity of the ferment is produced: it is removed, dried in the sun, and preserved to effect fresh fermentations. An analysis of kephir-grains dried at 100° gave—

Water .....	11·21
Fat .....	3·99
Soluble peptone-like substances .....	10·98
Proteids soluble in ammonia .....	10·32
"      "      potash .....	30·39
Insoluble residue .....	33·11

Microscopic examination of the insoluble residue showed it to consist of a mixture of yeast-cells with Kern's "*Bacterium dispora caucasica*." In a few cases, *Lepthothrix* and *Oidium lactis* were also observed. The whole of the active matter of the ferment was contained in the insoluble residue. From fermentation experiments made by the author, it appears that the yeast-cells alone are essential to the fermentation, the *Bacterium dispora caucasica* taking no part whatever in the action. The yeast-cells have been modified to a certain extent by having grown in contact with the leather of the bottles, and thus rendered capable of exciting the peculiar kephir-fermentation. A. J. G.

**Improvements in the Manufacture of Sugar.** (*Dingler*, 252, 287—293.)—Steffen's defecation process for obtaining sugar from molasses is conducted in the following manner:—Molasses or syrups are diluted with cold water in vessels fitted with agitators. The temperature of the solution should not exceed 35°, and its con-

centration should correspond with 6—12 per cent. of sugar. A known quantity of this solution is run into a vessel provided with an agitator and treated with from 50 to 100 parts of powdered lime to each 100 of sugar, to form calcium saccharate. The mixture is passed through filter-presses and the solution of calcium saccharate collected in suitable vessels; to 100 parts of sugar contained in this filtrate, about 65 parts of lime are then added for the separation of the insoluble saccharate, which is washed and decomposed in the usual way.

To facilitate the use of half-shadow saccharometers, Allary, instead of illuminating the polarising apparatus, proposes to enclose it in a black paper cylinder, the circular opening of which is covered with translucent yellow paper or with yellow glass. The observer covers his head and the whole apparatus with a black cloth and places the tube in the direction of a light wall. The reading of the degrees is effected in daylight.

Stuckenberg (Ger. Pat., 25,218, May, 1883) has found that in the production of strontia-sugar from molasses by Scheibler's process, the excess of strontium hydroxide necessary to effect the separation of strontium disaccharate acts essentially as free alkali. Since strontium disaccharate is almost insoluble in alkaline solutions, the excess of strontium hydroxide may be replaced by potassium or sodium hydroxide.

D. B.

**Adulteration of Verdigris.** By M. ASTRE (*J. Pharm.* [5], 7, 386—388).—The author has found that a commercial specimen of verdigris was adulterated to the extent of about 10 per cent. with a siliceous earth coloured by Prussian blue.

W. R. D.

**Abridged Process for Turkey-red Dyeing and Printing with Alizarin.** By A. MÜLLER (*Dingler*, 252, 219).—It is known that a number of the volatile organic ammonia bases produce precipitates with alkyl radicles, alumina (and tin), and saline solutions, which dissolve in an excess of the precipitant, for instance, mono-, di-, and tri-ethylamine, butyl- and amyl-amine, and di- and tri-amines. The author utilised this property experimentally in order to combine the mordanting of the fabric with oil and alumina in one operation, whereby the chalk-bath necessary at other times is omitted, the fabric being ready to receive the alizarin after it has been dried and the base removed by volatilisation. A clear saturated solution of aluminium hydroxide in 10 per cent. ethylamine was treated with about 15 per cent. Turkey-red oil neutralised with ethylamine. The fabric after being boiled and dried was treated with the clear mordant and dried at the ordinary temperature. It was then dyed with alizarin and soaped, a bright red colour being obtained.

The author is of opinion that if it were possible to prepare ammonias of the above type cheaply on a large scale, the success of this method would be established, especially if the volatile bases employed could be recovered by some suitable arrangement.

D. B.

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## General and Physical Chemistry.

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**Infra-red Radiation Spectra of Metallic Vapours.** By H. BECQUEREL (*Compt. rend.*, **99**, 374—376).—The metals were volatilised in the electric arc, and the spectra, obtained by means of a Rutherford's grating or a carbon bisulphide prism, were projected on a screen covered with some phosphorescent substance (*Abstr.*, 1883, 761). A table is given showing the wave-lengths of a number of lines in the infra-red spectra of potassium, sodium, strontium, calcium, magnesium, aluminium, zinc, cadmium, lead, thallium, bismuth, silver, and tin. C. H. B.

**Chemical Action of Light.** By D. AMATO (*Gazzetta*, **14**, 57—72).—The author has long held the opinion that many reactions which are said to take place through the direct action of light are not due entirely to that cause, but that light acts only under certain determinate conditions of temperature; consequently, there are limits of temperature within which light does not act in this way. In support of this opinion, the author has made numerous experiments, which are given in detail in the paper.

It is usually stated in text-books that light acts on liquid hydrogen phosphide, and decomposes it into solid and gaseous hydrogen phosphides. The author found, however, that inflammable gaseous hydrogen phosphide (containing liquid phosphide) loses its property of taking fire spontaneously on contact with the air, if kept over water *in the dark* for 24 hours at a temperature of 10—12°, whilst the same gas confined over mercury remains unchanged. It was proved that this decomposition is due to the oxygen dissolved in the water. At a temperature of 29°, and exposed to diffused light, gas confined over mercury was decomposed with deposition of solid hydrogen phosphide, whilst the same gas, if kept at 10°, was not decomposed, even when exposed to the brilliant July sunlight of Italy. In another experiment, in which the gas was exposed to the full heat of the sun (39°), whilst the light was completely excluded by a black varnish (made with glue and lampblack), the gas was not acted on. From this it would seem that neither the most brilliant sunshine (at temperatures below 10°) or heating to a temperature of 39°, are individually capable of effecting the decomposition of liquid hydrogen phosphide, but that this takes place readily by the joint action of sunlight and heat.

Similar experiments were made with a mixture of chlorine and hydrogen, and it was found that, if cooled to -12°, it could be exposed to the direct rays of the sun for hours without combination taking place. Care, however, must be taken that the chlorine is not exposed to the sun's rays even for an instant *before cooling*, as insolation renders chlorine capable of combining with hydrogen even in the dark. At a temperature of 39°, there is no action if light is excluded.

Silver chloride, if cooled to  $-12^{\circ}$ , is not acted on by the direct solar rays, but if allowed to get warm, decomposition begins immediately. Paternò has also observed that chlorine and ethylene do not combine in diffused light if the temperature is low, or only very slowly.

Another substance which is usually supposed to undergo decomposition on exposure to light is Fehling's test. The author finds, however, that this change is due to dust from the atmosphere, and the fact of keeping the bottle containing the solution wrapped up in paper and in a cupboard preserves it, merely inasmuch as it keeps it comparatively free from dust. If the solution be boiled in a narrow-necked flask for some hours, and after being allowed to settle, the clear liquor is decanted into a clean well-stoppered bottle, it may be exposed for any length of time to the direct rays of the sun without undergoing any change. In order to ensure success, the bottle should be rinsed out successively with permanganate solution and distilled water before introducing the Fehling's test. In order to prove that the dust in the air is the cause of decomposition, two samples prepared as above were taken, and through one of them a current of air from the laboratory was passed previously to closing the bottle. After exposure to light for a year, cuprous oxide was deposited in the solution contaminated with dust from the air, whilst the other remained unchanged.

The author has also noticed that solutions prepared in the ordinary way, after being kept for some time—a year or more—yield an abundant deposit of cuprous oxide if cautiously neutralised with sulphuric acid, and this even in the cold, but more readily when heated. A solution recently prepared, or one treated in the manner above described, does not behave in this way.

From these experiments the author concludes that—at all events for the substances above mentioned—light acts only under certain conditions as to temperature, and heat only under the influence of light, and that neither of them acts in the absence of the other.

C. E. G.

**Electricity of Flames.** By J. ELSTER and H. GEITEL (*Ann. Phys. Chem.*, **22**, 123—127).—This paper is a reply to a communication of Kollert's on the same subject (this vol., 651). The authors think that Kollert has overlooked the results of their investigation on "The Development of Electricity by the Contact of Gases with Incandescent Bodies" (*Ann. Phys. Chem.* [2], **19**, 558), by which they show that the so-called electricity of flames is merely a special case of a much more general class of phenomena, namely, that gases in contact with any incandescent substances become positively electrified. Thus the stratum of air surrounding the flame has a positive charge, which in Kollert's mode of experimentation affects the indications of the electrometer, which also are liable to be modified by the electrical condition of the air of the room. The present paper gives determinations made by the author's arrangement of the electrodes after the air of the apartment had been electrified to a high potential, sometimes positively and sometimes negatively, by means of an electrical machine. The observed value of the flame potential



was independent of this condition and nearly constant, having a mean of 0.65 Daniell. A flame is regarded by the authors as merely a current of heated gas, which negatively electrifies the incandescent bodies in contact with it, or the incandescent particles it may contain.  
R. R.

**A New Cell founded on the Oxidation of Carbon in the Cold.** By A. BARTOLI and G. PAPASOGLI (*Gazzetta*, 14, 85—90).—The authors allude to their experiments on the electrolysis of different liquids, using carbon electrodes, in which the latter were attacked, giving rise to organic compounds, such as mellic and hydromellic acids, mellogen, &c. (Abstr., 1882 and 1883). From thermochemical considerations, they were led to determine the electromotive force of different varieties of carbon in contact with platinum and gold; and the results of these measurements were so favourable, that they were enabled to construct a cell, somewhat feeble, but still sufficiently constant to be used for several months for working electric bells.

Experiments were made with electrodes of gold or platinum, and gas-carbon, charcoal, or graphite, using sulphuric, hydrochloric, acetic, nitric, and chromic acids; also solutions of sulphates, nitrates, chromates, and permanganate, and in all cases the electromotive force was appreciable. The carbons employed were rather long, only about one quarter of their length being immersed in the liquid, and every care was taken to guard against polarisation currents.

With solutions of sodium or potassium hydroxide, sp. gr. 1.1 to 1.3, platinum and different specimens of gas-carbon and charcoal, the electromotive force varied from 0.06 to 0.17 Daniell, after 24 hours' immersion. With solutions of sodium and potassium carbonate, the electromotive force was feeble, but amounted to 0.10 to 0.17 Daniell if the carbons had been previously saturated with a solution of the hydroxide.

Strong solutions of sodium hypochlorite, made by decomposing "chloride of lime" with sodium carbonate, gave an electromotive force equivalent to 0.4 to 0.5 Daniell after 24 hours' immersion. With graphite, it was rather less. Gas-carbon *by itself* is not attacked even by concentrated solutions of alkaline hypochlorites, but the action commences immediately if contact is made with a plate of platinum or gold immersed in the liquid. Are-light carbons were entirely disintegrated and destroyed in a month's time, the solution becoming deep yellow, and containing mellic acid and other benzenecarboxylic acids. Calcium hypochlorite gives similar results, but the electromotive force is less, varying from 0.10 to 0.20 Daniell.

The influence of temperature on the cell was also studied in a gold | gas-carbon element, with sodium hypochlorite: the electromotive force varied from 0.18 to 0.27 Daniell, as the temperature was raised from 14° to 100°.

By modifying the conditions, surrounding the platinum pole with a solution properly chosen, and separated from the hypochlorite by a porous septum, the authors have arranged a cell which remains practically constant for months.  
C. E. G.

**Battery with Carbon Electrodes.** By D. TOMMASI and RADIGUET (*Compt. rend.*, **99**, 129—130).—This battery consists of a rectangular porcelain cell, on the bottom of which is placed a carbon plate surrounded by a paste of lead peroxide, which constitutes the positive pole. Above this is another plate of carbon, on the upper surface of which are placed pieces of gas-carbon, the two plates being separated by parchment paper, which divides the cell into two compartments. A small quantity of a saturated solution of common salt is poured into each of the compartments in such a way that the lead peroxide is not disintegrated, and the fragments of gas-carbon on the second plate are only partially covered. The electromotive force of the pile is 0.6 volt, and is not sensibly altered by the substitution of a solution of ammonium sulphate or chloride, or sodium sulphate, or even dilute sulphuric acid, for the sodium chloride. C. H. B.

**Galvanic Batteries for the Electric Light.** By I. PROBERT (*Dingl. polyt. J.*, **253**, 252).—From a comparison of the cost of producing the electric light by means of dynamo-machines and galvanic batteries, the author infers that for working the light on a large scale, galvanic (primary) batteries have no prospect of success. A reduction in the cost of batteries suitable for the illumination of houses may be possible in four directions:—(1) by substituting cheaper metals for zinc, *e.g.*, lead or iron; (2) by employing hydrochloric acid in the place of sulphuric acid; (3) by completely exhausting the solution; and (4) by recovering valuable bye-products.

In referring to primary batteries, the author states that Holmes and Burke's element consists of eight cells filled with sodium nitrate dissolved in dilute sulphuric acid. It is provided with a syphon arrangement for filling and emptying the cells and conducting the gaseous products to a vessel, where they are dissolved or absorbed. The hydrogen decomposes the sodium nitrate, sodium sulphate and nitric acid being formed. The electrodes are carbon and amalgamated zinc. In Ross's element each cell contains two carbon plates, which are placed in dilute hydrochloric acid. To the latter a substance called "eureka" is added, the composition of which is kept secret. In the Edco or Heap battery, zinc carbons and potassium dichromate are the depolarisers, and dilute sulphuric acid is the exciting agent. The cells are lined with lead, their capacity being equal to 6.75 litres (1.5 galls.). The cost of the solution amounts to one shilling per gallon. The zinc plates are 254 mm. long and 152 mm. wide, and weigh 1.36 kilos. The E.M.F. is equal to 2 volts and the resistance 0.2 ohm. The zinc plates in Oliphant, Burr, and Gowan's battery are coated with a thin film of gold before amalgamation, whereby a diminution in the local action is said to be effected. D. B.

**Conversion of Liquid Batteries into Dry Piles.** By ONIMUS (*Compt. rend.*, **98**, 1577—1578).—Batteries containing solution of ammonium chloride, zinc chloride, &c., may be converted into dry piles by mixing these solutions with plaster of Paris and allowing the mixture to solidify. If mixtures of ferric oxide or manganese

peroxide with plaster of Paris are employed, the electromotive force is slightly higher than with plaster of Paris alone, and when ferric oxide is used the battery quickly regains its original electromotive force when the circuit is broken. When the battery is exhausted the solid plaster is simply again moistened with the solution.

C. H. B.

**Electrolysis of Solid Glass.** By E. WARBURG (*Ann. Phys. Chem.*, **21**, 622—646).—When calcium sodium glass is submitted to electrolysis at a temperature of  $300^{\circ}$  between electrodes of mercury, a badly conducting film of  $\text{SiO}_2$  separates at the anode, and in a short time reduces the intensity of the current to a small fraction of its original value. This film has a greater or less thickness according as a greater or less electromotive force has been in operation for a given time. It acts like the dielectric of a condenser between plates, one of which is the conducting part of the glass and the other the mercury of the anode. The capacity of this condenser is independent of the difference of potential between its conducting surfaces, and it varies from 1 to 20 B.E. But when sodium amalgam is substituted for the mercury at the anode, the same weight of sodium is taken up by the glass as is liberated at the kathode, so that the weight of the glass remains unchanged, and its transparency and other properties are not perceptibly affected by the electrolysis.

R. R.

**Electrical Conductivity of Distilled Water and of Ice.** By G. FOUSSEREAU (*Compt. rend.*, **99**, 80—82).—The specific resistance of distilled water at  $15^{\circ}$  was found to vary between 118,900 ohms and 712,500 ohms, the maximum being obtained with water which had been redistilled two or three times in a platinum apparatus. The resistance of water kept in a glass vessel at about  $15^{\circ}$  diminishes by about one-thirtieth after 24 hours, owing to the solvent action of the water, and the diminution is very much more rapid at higher temperatures. If the water is kept in platinum vessels exposed to the air, its resistance diminishes slowly, owing to the solution of the small quantity of salts and acid vapours present in the atmosphere. Carbonic acid has but little effect on the conductivity. In many cases the resistance of distilled water is affected by small quantities of dissolved substances carried over during distillation.

The variation in the resistance of distilled water with the temperature between  $0^{\circ}$  and  $21^{\circ}$  is represented with great accuracy by Poiseuille's formula for the variation of the internal friction,  $1 + at + bt^2$ , or, in other words, the resistance of distilled water is proportional, within certain limits, to the coefficient of internal friction.

The resistance of water becomes 15,000 times greater at the moment of congelation, the specific resistance of ice varying between 4865 megohms at  $-1^{\circ}$ , and 53,540 megohms at  $-17^{\circ}$ . The resistance of ice shows variations corresponding with the resistance of the water from which it was formed.

C. H. B.

**Electrical Conductivity of Dilute Solutions.** By E. BOUTY (*Compt. rend.*, **99**, 30—32).—Many organic substances do not sensibly

diminish the resistance of distilled water, whilst even those which are the best conductors have a resistance from 50 to 200 times as great as that of neutral salts.

Anhydrous acids and alkalis are non-conductors; hydrated acids and alkalis conduct in the same manner as salts.

Organic alkalis in dilute aqueous solution have a resistance 600 to 800 times as high as that of salts; and ammonia, which forms no definite compound with water, has a resistance 110 times as great as that of salts. On the other hand, potassium, sodium, barium, calcium, lithium, and thallium hydroxides are good conductors. The ratio of the resistance of a solution of potassium hydroxide to that of an equivalent solution of potassium chloride, for example, is about 0.4, but the ratio is higher the more dilute the solution.

An aqueous solution of arsenious anhydride is practically a non-conductor, and solutions of carbonic anhydride and hydrogen sulphide have a resistance far higher than that of salts. None of these substances form definite compounds with water. A solution of sulphurous anhydride at 20°, on the other hand, has a resistance only 2.33 times as great as that of an equivalent solution of potassium chloride. The conductivity of the acid solution decreases much less than that of the salt solution when cooled down to 0°, probably owing to the formation of a further quantity of a hydrate. The resistance of dilute solutions of sulphuric acid varies in a complex manner with the degree of dilution, but is never more than about one-third of the resistance of an equivalent salt solution. The different inorganic and organic acids furnish every degree of conductivity between the non-conductor arsenious anhydride and the good conductor sulphuric acid. Boric acid and pyrogallol have a resistance as high as arsenious oxide, whilst nitric, hydrochloric, and picric acids conduct almost as well as sulphuric acid.

C. H. B.

**Compounds obtained by Means of Gas Batteries and the Silent Discharge.** By A. FIGUIER (*Compt. rend.*, **98**, 1575—1577).—The apparatus employed consisted of two hollow graphite cylinders closed at one end, and coated internally with spongy metal or spongy carbon so as to prevent polarisation. These cylinders were supported by a lid which closed hermetically the vessel containing the liquid conductor, the latter being alkaline when the product of the reaction was acid, and *vice versâ*. In some cases the gases were subjected to the silent discharge before being placed in the battery. The compounds produced are formed in contact with the poles, and in greater abundance at the positive pole. Although the current produced may be very feeble, the energy of the reaction may be relatively large. In the following table the substance placed second constituted the positive pole:—

Air and sulphurous anhydride produce	sulphuric anhydride.
Hydrogen and chlorine	„ hydrochloric acid.
Oxygen and chlorine	„ chloric acid.
Nitrogen and oxygen	„ nitric anhydride.
Hydrogen and nitrogen	„ ammonia.

Carbonic oxide and sodium carbonate	produce	sodium oxalate and formate.
Ethylene and oxygen	„	formic and acetic acids.
Hydrogen and carbonic anhydride	„	formic and acetic acids.
Methane and carbonic anhydride	„	acetic acid.

The ozonisers employed were provided with armatures coated with platinum black, and were so arranged that their temperature could be raised. Under the influence of the discharge oxygen combines directly with sulphur, selenium, chlorine, iodine, and bromine, but has no action on tellurium. Hydrogen combines with sulphur, selenium, ordinary phosphorus, and nitrogen, but has no action on tellurium, arsenic, antimony, and red phosphorus. Oxygen oxidises formic acid and formates, carbonic oxide combines with hydroxides, &c.

C. H. B.

**Action of the Induction Spark on Benzene, Toluene, and Aniline.** By A. DESTREM (*Compt. rend.*, 99, 138).—The spark from a coil of moderate size worked by three Bunsen cells was passed into the liquids between platinum points placed very close together, and the gaseous products of decomposition were collected and analysed:—

*Benzene* yields acetylene 42—43; hydrogen 57—58 = 100.

*Toluene* „ „ 23—24; „ 76—77 = 100.

*Aniline* „ „ 21; hydrogen, 65; hydrocyanic acid, 9; nitrogen, 5 = 100.

Carbon is also liberated in a bulky form, that from the aniline being considerably more dense than that from the other two compounds. Benzene and toluene yield some diphenyl and a brown-red compound soluble in the hydrocarbons.

C. H. B.

**New Method of directly Measuring Absolute Magnetic Intensity.** By A. LEDUC (*Compt. rend.*, 99, 186—187).—A modified form of the manometer of Lippmann's galvanometer (this vol., p. 881) is employed. A current of from 1 to 3 amperes is passed through the manometer, and the latter is placed in the magnetic field, the intensity of which is measured by the rise or fall of the mercury in the arm of the manometer.

C. H. B.

**Magnetism of Organic Bodies.** By S. WLEÜGEL and S. HENRICHSSEN (*Ann. Phys. Chem.*, 22, 121—123).—The authors have examined the magnetism of compounds of the  $C_nH_{2n+1}$  alcohol radicals. The results show that the molecular magnetism is increased by a nearly constant amount for each  $CH_2$  in the compound, and that it is equal to the sum of the partial magnetism of the alcohol radicals and that of the remaining parts of the compound. In the compounds the specific magnetism is nearly the same for OH, I, Br, and S, but for Cl it is much greater. Propyl alcohol and isopropyl alcohol show exactly the same value, whilst isobutyl alcohol has the value found by calculation for butyl alcohol. For H in alcohol radicals, the value — 780·5 is found, whereas C has only — 5·6. The latter value is so insignificant compared with the former, that the observed results agree nearly as well with  $C = 0$ ,  $H = -807·6$ .

R. R.

**Specific Heat of Mellite.** By A. BARTOLI and E. STRACCIATI (*Gazzetta*, **14**, 105—114).—Three well-crystallised examples of mellite were examined: the first, from Bohemia, had a sp. gr. of 1.60; the second, from Artern in Thuringia, was of sp. gr. 1.57, and the third from Malanka in the Urals, of sp. gr. 1.59. The results of the analysis in each case corresponded with the formula  $C_{12}Al_2O_{12} + 18H_2O$ . The specific heat of the specimens was determined between the temperatures of 80° and 0° in three several ways: namely, with Bunsen's calorimeter, with a water calorimeter, and by Kopp's method. Full details of the experiments are given, and the results tabulated. The mean of the results is as follows:—

Bohemian mellite, by Bunsen's calorimeter, between 0° and 79° = 0.33005.

Bohemian mellite, by the water calorimeter, between 47° and 79° = 0.32816.

Thuringian mellite between 25° and 79° = 0.33155.

Uralian mellite between 27° and 79° = 0.33489.

Mellite by Kopp's method between 15.5° and 69° = 0.33592.

The mean of all these gives the number 0.33211.

By means of Person's formula (*Gazzetta*, **8**, 429), the approximate value 0.20958 is deduced for the specific heat of anhydrous mellite,  $C_{12}Al_2O_{12}$ .  
C. E. G.

**Thermal Effect of Mixing Liquids.** By KONOVALOFF (*Bull. Soc. Chim.*, **41**, 340).—The thermal effect of mixing liquids depends on the cohesive energy of each liquid, indicated by the heat of vaporisation and on the degree of disaggregation, that is to say, upon the relative quantities of the two liquids. This view is confirmed by the existence of liquids which, when mixed, give rise either to an absorption or evolution of heat depending on their relative quantities. The former effect ensues in the solution of a liquid of great cohesive energy. The author agrees with the statement of Dossios, that solution may be regarded as the result of a strain between the force of molecular cohesion of homogeneous and heterogeneous liquids, but does not attribute an absolute character to the cohesive force.

W. R. D.

**Thermal Effect of Solution.** By ALEXÉEFF (*Bull. Soc. Chim.*, **41**, 256).—In the case of liquids, solubility is always attended with an absorption of heat if the substances do not react with each other. Solution is thermally distinguished from mixture by the fact that in the latter instance thermal absorption reaches the maximum when the liquids are present in equal proportions. Thus aniline with

5 per cent. of benzene	=	— 26.5 cal.
32       "       "	=	— 154       "
48.4     "       "	=	— 182       "
77       "       "	=	— 145       "
91       "       "	=	— 51       "

But when solution occurs the amount of heat absorbed increases as the quantity of substance dissolved becomes greater. Thus the solu-

tion of 1.85 parts of aniline in 100 parts of water is equal to  $-5$  cal., and when the quantity of aniline is raised to 97.01 parts the thermal effect is equal to  $-228$  cal.

W. R. D.

### Displacement of Chlorine by Bromine in Silver Chloride.

By T. S. HUMPHIDGE (*Ber.*, 17, 1838—1839).—Before becoming acquainted with Potilitzin's work on this subject (this vol., 955), the author had observed a displacement of chlorine by bromine in silver chloride even at the ordinary temperature. Freshly precipitated and well washed silver chloride was covered with bromine-water, and allowed to stand for some time: after 24 hours at  $11^{\circ}$ , 5.28 per cent.; after 76 hours at  $11.9^{\circ}$ , 10.15 per cent.; after 7 hours at  $44.4^{\circ}$ , 11.28 per cent.; and after 12 hours at  $44.4^{\circ}$ , 14.53 per cent. of chlorine had been displaced by bromine. The author points out that these results are even more opposed to Berthelot's "principe du travail maximum" than those given by Potilitzin, who employed higher temperatures. The author undertook these researches and is continuing them, for the purpose of throwing light on the influence of time, temperature, and mass in chemical reactions.

L. T. T.

### Thermochemical Researches on Fluorine Compounds.

By GUNTZ (*Ann. Chim. Phys.* [6], 3, 1—66).—In this memoir are collected the author's various determinations on the heats of combination, formation, and solution of the metallic compounds of fluorine; a greater part of the work has already appeared in abstract (*Abstr.*, 1881, 5, 544—546, 704, 884). A few incidental points of interest are alluded to in the course of the memoir.

Potassium fluoride is described by Berzelius as having an alkaline reaction; the perfectly dry salt is however quite neutral, and its alkalinity in aqueous solution is due to a slight loss of acid during evaporation, and the consequent formation of free alkali. As the heat of formation of potassium hydrogen fluoride is considerable, the author examined its degree of dissociation in dilute solution by causing to react together various proportions of potassium fluoride, hydrofluoric acid, and water; the results were—

KF (1 eq.) with HF (1 eq.) in 4 kilos. water, absorbs  $-0.33$  cal.

KF " " HF ( $\frac{5}{2}$  eq.) " " "  $-0.36$  "

KF " " HF (5 eqs.) " " "  $-0.78$  "

The heat of absorption increases with increase in the proportion of acid; the results of the converse reaction were—

HF (1 eq.) with KF (1 eq.) in 4 kilos. water, absorbs  $-0.33$  cal.

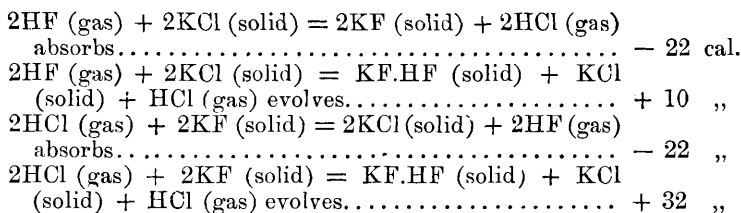
HF " " KF ( $\frac{5}{2}$  eq.) " " "  $-0.36$  "

HF " " KF (5 eqs.) " " "  $-0.54$  "

The same phenomenon is here noticeable, and thus the presence of an excess of one or other of the components modifies the chemical equilibrium and increases the proportion of constituents combined, a result analogous to that obtained by Berthelot and P. de Saint Gilles in their researches on etherification.

The interaction of hydrofluoric acid with potassium chloride, and of

hydrochloric acid with potassium fluoride, was also studied with the following results :—



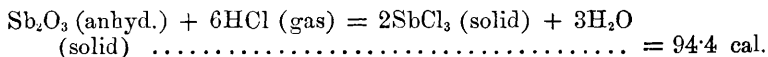
These experiments show that the hydrochloric acid is converted into the chloride, in presence of excess of fluoride, while the liberated hydrofluoric acid forms potassium hydrogen fluoride; whilst, in presence of excess of chloride, the hydrofluoric acid is gradually converted into potassium hydrogen fluoride, but on account of the decomposition of this salt by water the change is limited to one-fifth of the theoretical quantity.

On comparing the heats of neutralisation of various bases with hydrochloric, hydrofluoric, and sulphuric acids respectively, it is seen that the values for hydrofluoric and sulphuric acids are far closer to one another than those of hydrochloric and hydrofluoric acids.

Determinations of the heat of formation of the chloride and oxychloride of antimony are also given, and an investigation on the fluosilicates (cf. Abstr., 1884, 884).

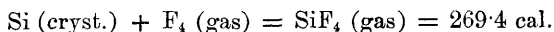
*Antimony trichloride* is decomposed by water with formation of the oxychlorides,  $\text{SbO}_2\text{Cl}$ ,  $\text{Sb}_2\text{O}_3\text{Cl}$ , and the hydrated oxide. The heat of neutralisation of antimonious oxide was determined either by the direct solution of the oxide in hydrochloric acid, or indirectly by dissolving antimony trichloride in hydrofluoric acid, and comparing the heat evolved with that disengaged by the solution of an equivalent weight of antimonious oxide in hydrofluoric acid.

The mean result of these two independent methods was—

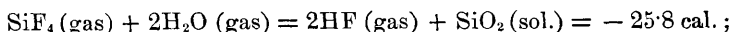


It was found that the decomposition of antimony chloride by water does not give exactly the oxychloride  $\text{Sb}_2\text{O}_3\text{Cl}$ ; definite equilibrium is established only after a long interval of time.

*Silicon Fluoride*.—From Thomsen's data of the heat of solution of silicon in hydrofluoric acid, and of silicon fluoride in water, the author calculates for the heat of formation of silicon fluoride :



The action of steam on silicon fluoride with formation of hydrofluoric and silicic acids is an endothermic change :



consequently it can only take place provided that the temperature is sufficiently high to prevent the secondary reaction, viz., combination



of hydrofluoric acid with water, and formation of hydrofluosilicic acid, which develops an amount of heat sufficient to compensate the absorption. This theoretical deduction is completely in accordance with the experiments of Hautefeuille, who demonstrated that silicon fluoride is not decomposed by steam above  $150^{\circ}$ . V. H. V.

**Combustion of Explosive Gases in various States of Dilution.** By A. WITZ (*Compt. rend.*, **99**, 187—190).—The heat developed by the explosive combustion of water-gas, mixed with twice its volume of oxygen, is notably less than that developed by the explosion of water-gas alone, and the difference is greater when carbonic anhydride is substituted for oxygen. C. H. B.

**Non-existence of Ammonium Hydroxide.** By D. TOMMASI (*Bull. Soc. Chim.*, **41**, 444—445).—The author points out that there is a great discrepancy between the calculated and experimental heat of formation of ammonium hydroxide. The former is  $54\cdot2$  cal., but the latter only 21 cal., whereas the heats of formation of other hydroxides (sodium, lithium, calcium, &c.) determined experimentally, agree with the calculated results. From this the author concludes that a hydroxide of ammonium is not contained in the aqueous solution of ammonia-gas, or, more strictly, that the constitution of this solution differs from that of the other alkaline hydroxides.

W. R. D.

**Lithium Oxide.** By BEKETOFF (*Bull. Soc. Chim.*, **41**, 311—312).—The heats of formation of the oxides of lithium, sodium, and potassium were determined, and also the heats of hydration of the same oxides, with the following results, which are in accordance with the theoretical predictions of the author :—

	$M_2 + O.$	$M_2O + H_2O.$	$M_2O + Aq.$
Li .....	140,000	13,000	26,000
Na .....	108,000	35,400	55,000
K .....	97,000	42,000	67,000

Lithium oxide prepared by Troost's method always contains carbonate. When anhydrous lithium carbonate is dissolved in water, heat is evolved; moreover, the solubility of this compound decreases with an increase of temperature. These facts point to the existence of an unstable hydroxide. W. R. D.

**Mixed Liquids of Constant Boiling Point.** By D. KONOVALOFF (*Ber.*, **17**, 1531—1539).—In a former communication (*Abstr.*, 1881, 1093) the author showed that two miscible liquids form a mixture of constant boiling point when the vapour-tension curve (taken as a function of the composition of the mixture) has a maximum or a minimum. From a review of existing data, and an examination of many fresh mixtures, the author now draws the following conclusions.

i. When the vapour-tension curve of a mixture of constant boiling point has a minimum (*i.e.*, when the vapour-tension of the mixture is less than that of either of the constituents), the constituent of lower

boiling point preponderates in the mixture. ii. When the tension-curve shows a maximum (*i.e.*, exceeds that of either of the constituents), the liquid of greater vapour-tension forms the larger proportion of the mixture. iii. The ratio between the two constituents of a mixture of constant boiling point approaches more nearly to equality the nearer together their vapour-tensions are in the free state; and diverges more from equality the further apart their vapour-tensions are. iv. The greater the mutual action of the two liquids on one another, the greater is the tendency to the formation of a mixed liquid having a minimum curve.

L. T. T.

**Different Methods of Distillation compared.** By H. KREIS (*Annalen*, **224**, 259—269).—A series of quantitative experiments on fractional distillation shows that the best results are obtained for mixtures boiling about 100° by using Linnemann's tubes (*Annalen*, **160**, 195), or the simpler and less expensive apparatus devised by Hempel (*Zeits. Anal. Chem.*, **20**, Part IV). A flask provided with a bulb on its neck yields better results than a long-necked flask for mixtures boiling about 300°.

W. C. W.

**Production of very Low Temperatures by Means of Methane.** By L. CAILLETET (*Compt. rend.*, **98**, 1565—1566).—When methane is slightly compressed, and cooled by means of liquid ethylene boiling under ordinary atmospheric pressure, it condenses to a colourless very mobile liquid, and if this liquid methane is allowed to boil under atmospheric pressure the temperature produced is sufficiently low to liquefy oxygen immediately.

C. H. B.

**The Freezing Point of Saline Solutions.** By F. M. RAOULT (*Compt. rend.*, **99**, 324—326).—Determinations of the freezing points of solutions of salts of polyatomic metals which are not decomposed by water give the following results:—

	Molecular weight.	Reduction of freezing point by 1 gram of salt in 100 grams of water.	Molecular reduction.
Stannic chloride . . . . .	260	0·370	96·3
Aluminium chloride . . .	268	0·481	129·0
Chromic chloride (violet)	318	0·408	130·0
Ferric chloride . . . . .	325	0·396	129·0
Aluminium nitrate . . .	283	0·458	129·8
Chromic nitrate (violet).	333	0·384	128·0
Aluminium sulphate . . .	343	0·129	44·4
Chromic sulphate (violet) . . . . .	393	0·115	45·4
Ferric sulphate . . . . .	400	0·115	46·0

From these results, and others previously obtained (this vol., pp. 701 and 808), it follows that—

(1.) When in a solution of a salt of a monovalent metal containing 1 equivalent of the metal in 100 grams of water, the monovalent metal is replaced by an equivalent quantity of a bivalent or multivalent

metal, the molecular reduction of the freezing point is diminished by a practically constant quantity, about 10·5.

(2.) When in a solution of a salt of a strong monobasic acid containing 1 equivalent of the acid in 100 grams of water, the monobasic acid is replaced by an equivalent quantity of a strong dibasic acid, the molecular reduction of the freezing point is likewise diminished by a practically constant quantity, about 14.

The sums and differences of the partial reductions of the freezing point by saline radicles being thus known, it is possible to calculate the absolute values of these reductions if it is admitted that there is a constant ratio between the partial reductions produced by electronegative and electropositive radicles of the same atomicity. It is thus found that the partial reductions caused by saline radicles approximate to the following values:—

	Partial molecular reduction.
Univalent electronegative radicles (Cl, Br, OH, NO <sub>3</sub> , &c.)	20
Bivalent       "       "       "       (SO <sub>4</sub> , CrO <sub>4</sub> , &c.) ....	11
Univalent electropositive       "       (H, K, Na, &c.) ....	15
Bi- or multivalent electropositive radicles ..... (Ba, Mg, Al <sub>2</sub> ) .....	8

From these data it is possible to calculate approximately the molecular reduction of the freezing point caused by the majority of salts formed by the union of a strong acid with a strong base. The values thus obtained agree very closely with the results of experiment, and it follows that *the molecular reduction of the freezing point, produced by salts formed by the monobasic and bibasic acids, is sensibly the sum of the partial molecular reductions of the electropositive and electronegative radicles*. These facts prove that, contrary to the author's previous belief, the *general law of congelation* is not applicable to salts dissolved in water, and they justify the criticisms of Debray (*Compt. rend.*, 1883, 97, 825). It would seem, however, that this law is applicable to the constituent radicles of the salts, almost as if these radicles were simply mixed in the solutions, and this constitutes further evidence that the radicles of salts dissolved in water act independently in modifying the physical properties of the solvent. C. H. B.

**Absorption of Chlorine by Carbon, and its Combination with Hydrogen.** By BERTHELOT and GUNTZ (*Compt. rend.*, 99, 7—8).—Melsens found that when hydrogen is passed over purified wood-charcoal saturated with chlorine, hydrochloric acid is formed, but there is a reduction of temperature. The authors find that the absorption of 35·5 grams of chlorine by purified charcoal develops + 6·78 cal., a quantity almost double the heats of volatilisation of liquid bromine and iodine, but still considerably below the heat of formation of hydrochloric acid. When, however, hydrogen is passed over the charcoal saturated with chlorine, hydrochloric acid is formed, and a considerable proportion of the absorbed chlorine is given off unchanged. The amount of chlorine thus given off is seven times as great as the volume of hydrochloric acid formed, the heat

absorbed by the first change is greater than that developed by the second, hence the reduction of temperature. C. H. B.

**Behaviour of Vegetable Tissues, Starch, and Charcoal, towards Gases.** By J. BÖHM (*Bied. Centr.*, 1884, 316—319).—Experimenting with cork and pine-wood, the author found that the first portions of the gas removed from them in a vacuum contained from 6 to 12 per cent. more oxygen than common air; raspings of wood or cork did not absorb hydrogen or oxygen, and the same was found to be the case with pine-wood, which was easily permeated by air under pressure, as also was deal which had lain long in water, and was, therefore, to some extent, decayed. As the tissue of wood contains air rich in oxygen, it follows that this gas must diffuse more readily through the walls than nitrogen. Carbonic anhydride is absorbed in quantities which vary in proportion with the amount of aqueous vapour present, cork powder absorbing less than wood. Starch absorbs most carbonic anhydride when perfectly dry, and the gas is not wholly removable in a vacuum, but completely by immersion in water. Charcoal condenses but a small amount of air, and that which is first removed is richer in oxygen than that which follows. Freshly-ignited charcoal absorbs many times its volume of air, and relatively more oxygen than nitrogen, the latter being completely removable, the former only partly by boiling water. Freshly-ignited coal absorbs neither nitrogen nor hydrogen, but some carbonic anhydride and much oxygen, which probably is employed in oxidising hydrocarbons. E. W. P.

**Coagulation of Colloids.** By E. GRIMAUZ (*Compt. rend.*, 98, 1578—1581).—Colloids may be divided into two groups, according as their coagulation is prevented or hastened by dilution.

The first group includes ferric hydroxide, soluble silica, the nitrogenised colloids, albumin, and the amidobenzoic colloids, the coagulation of which requires a longer time or a higher temperature the more dilute the solution. In such cases, coagulation is analogous to etherification. Just as ethereal salts are formed with elimination of water, so ferric hydroxide and silicic hydroxide,  $\text{Si}(\text{OH})_4$ , undergo condensation with elimination of water, forming respectively in the first place such compounds as  $\text{Fe}_4\text{O}(\text{OH})_{10}$  and  $\text{Si}_2\text{O}(\text{OH})_6$ . Coagulation, like etherification, takes place very slowly at the ordinary temperature, especially if the solutions are dilute, but both changes are accelerated by the action of heat, and attain their maximum limit more quickly the higher the temperature. Salts which promote coagulation act as dehydrating agents, just as barium chloride impedes the saponification of ethyl benzoate (Berthelot). Coagulation, however, unlike etherification, is generally not reversible, but even here the difference is not absolute, for under certain conditions coagulated silicic or ferric hydroxide can redissolve in water, and, on the other hand, the decomposition of ethereal salts by water is never complete, whatever the proportion of water. The gradual contraction of the coagulum is due to a continuation of the process of condensation, with further elimination of water.

When coagulation is promoted by dilution, as in the case of ferric derivatives, Schweizer's reagent, calcium saccharate, &c., it is due to dissociation produced by the action of the water. This explanation is supported by the fact that in these cases coagulation by addition of water is impeded, or even entirely prevented, by the presence of an excess of one of the constituents of the colloïd. C. H. B.

**The Dehydrating Action of Salts.** By D. TOMMASI (*Compt. rend.*, **99**, 37—38).—Grimaux's researches on the coagulation of colloids lead to the conclusion that salts promote the coagulation of some colloids by acting as dehydrating agents. There are, however, cases in which certain salts produce an exactly opposite effect, and prevent the dehydration of other substances. The temperature required to convert cupric hydroxide into cupric oxide, for example, is higher in presence of sodium acetate, sulphate, and hydroxide, potassium bromide, chlorate, and iodide, than in pure water, and the presence of 10 per cent. of calcium chloride, of saccharose, and of even 0·3 per cent. of manganese sulphate, prevents the dehydration of cupric hydroxide, even at 100°. Potassium chloride, sodium carbonate, and stronger solutions (10 per cent.) of sodium hydroxide facilitate the conversion of cupric hydroxide into the oxide. C. H. B.

**Cohesion of Saline Solutions and of their Admixtures.** By O. ROTHER (*Ann. Phys. Chem.*, **21**, 576—615).—In his determinations of capillary cohesion, the author has made use of tubes of an elliptical section, which he has found very uniform in calibre, and in which the liquid rises to a greater height than in the more usually employed circular tubes of equal area of bore, thus admitting of more accurate measurements being made. He distinguishes the *actual cohesion* of each solution from the *specific cohesion*, the latter being obtained by referring the observed value to the molecular weight of the salt. The experimental results are shown in an extended series of tables, and a plate accompanies the paper, giving graphic representations of the determinations. Among the general laws proceeding from these, and fully discussed in the paper, the most interesting are, perhaps, the following:—The *actual cohesion* increases with the quantity of salt in the solution, being, in fact, a linear function of that quantity, and it is greater with salts of smaller molecular weights. Solutions containing equal percentages of  $K_2SO_4$  and of  $Na_2SO_4$  have the same *actual cohesion*. The *specific cohesion* increases more rapidly with the small than with the larger percentages of salt. Equal quantities of NaCl and of KCl, dissolved in equal quantities of water, give solutions of the same *specific cohesion*. The cohesion of solutions containing known quantities of one or more salts may be expressed in mathematical formulæ involving the capillary constants. R. R.

**Diffusion of Gases through a Porous Septum.** By G. HANSE-MANN (*Ann. Phys. Chem.*, **21**, 546—562).—The object of the researches recorded in this paper is to test the validity of the theory of the diffusion of gases through a porous septum, enunciated in 1871

by Stefan (*Wien. Akad. Ber.*, **63**, 111), who treats it as a particular case of his general theory of gas motion, in which he regards the porous substance as a gas with immovable particles. This theory involves the assumption that the free diffusion of the two gases in the very narrow spaces of the porous body takes place exactly as in larger spaces, but according to the author's results and deductions, this does not appear to be the case, and his experiments do not confirm Stefan's theory.

R. R.

**Colour of Chemical Compounds, mainly as a Function of the Atomic Weights of the Component Elements.** By T. CARNELLEY (*Ber.*, **17**, 2151—2156).—The colour of chemical compounds has been studied by Ackroyd, who drew the conclusions (I) that with increasing temperature the colour of a compound approaches more and more to the red end of the spectrum, and at a sufficiently high temperature passes into brown and black; (II) in binary compounds an increase in the amount of the electronegative element causes a change of colour towards the red end of the spectrum, and finally into brown and black. To these rules the author adds a third:—In a series of compounds,  $AxRy$ ,  $BxRy$ ,  $CxRy$ , &c., in which R is an element or group of elements, and A, B, C, &c., are elements belonging to the same sub-group in Mendelejeff's table of the natural classification of the elements, with the increasing atomic weight of the elements A, B, C, &c., the colour of the compound approaches the red end of the spectrum, and in many cases passes into brown and black. Of 426 substances examined only 14 exceptions to the last rule were found, and only four of these did not admit of explanation. The paper concludes with a theoretical explanation of the subject.

A. J. G.

**Specific Volumes of Liquids.** By W. LOSSEN and A. ZANDER (*Annalen*, **225**, 109—120).—This memoir, a continuation of former researches (*Abstr.*, 1882, 1259; 1883, 13), deals with observations of the coefficients of expansion and specific volume of additive compounds of the aromatic hydrocarbons. The results obtained are compared with previous determinations for olefine hydrocarbons metameric with them, and also with their isologues in the aromatic series. The following table contains a summary of results; in the first column is the name of the substance, in the second the observed boiling point, the third, fourth, and fifth the experimental values for  $a^{-4}$ ,  $b^{-6}$ ,  $c^{-9}$ , in the general equation  $V = 1 + at + bt^2 + ct^3$ , and in the sixth the specific volumes at the boiling point:—

Substance.	Boiling point.	$a^{-4}$ .	$b^{-6}$ .	$c^{-9}$ .	Sp. vol.
Hexahydrotoluene, $C_7H_{14}$ ....	96	11.436	0.43104	16.551	142.0
Hexahydroisoxylene, $C_8H_{16}$ ..	118	10.672	1.061	7.5268	164.8
Naphthalene, $C_{10}H_8$ .....	217.1	8.8962	0.56843	3.9971	147.2
Hexahydronaphthalene, $C_{10}H_{14}$ .....	200	8.2659	0.7227	1.4935	171.2

It has been remarked by Wreden that the sp. gr. of the additive compounds of the aromatic hydrocarbons is greater than that of the isomeric olefines; the presumable converse of this statement, viz., that the specific volume of the former is less than that of the latter, is confirmed, for the observed specific volume of hexa-hydro-isoxylene and -hydrotoluene are less by about 12·5 than those of their corresponding metamerides, caprylene and heptylene.

Cymene and hexahydronaphthalene are metameric, the specific volume of the latter derived from the benzene nuclei is 12·8 less than that of the former, containing one such nucleus, this difference being approximately equal to that observed between the olefines and their metamerides in the aromatic series.

In the table given in the memoir, the specific volumes of hydrocarbons containing the same number of carbon-atoms, but a different number of hydrogen-atoms, are compared; it is thus shown that the difference of specific volumes of isologues in the paraffin and the aromatic derivatives are approximately equal.

Thus toluene, xylene, and naphthalene are precisely to the same degree unsaturated hydrocarbons as amylene, styrene, and diallyl. This conclusion is in direct opposition to the observations of Schiff on the specific volume, and of Thomsen on the heat of combustion of benzene, which have tended to establish that in this hydrocarbon, each carbon-atom is united to three other carbon-atoms, and thus is formed a combination with affinities completely satisfied. V. H. V.

**A Hydrometer for Demonstrating Alterations in Weight in Chemical Changes.** By M. GREGER (*Ber.*, 17, 568—571).—A description of a sensitive hydrometer for lecture purposes, requiring the accompanying plates to be of service. P. P. B.

**Apparatus for Collecting Solid Carbonic Anhydride.** By DUCRETET (*Compt. rend.*, 99, 235—237).—The apparatus consists of a cylindrical ebonite receiver, provided with a hollow ebonite handle, and fitted with a cover which can be fastened by means of a bayonet joint. A tube, also of ebonite, is fixed obliquely in the cover, and passes down nearly to the bottom of the receiver. This tube is connected with the reservoir of liquid carbonic anhydride, and the latter strikes against the ebonite sides of the receiver. A much greater yield of the solidified gas is obtained than with the original Thilorier's apparatus. The displaced air and the evolved carbonic anhydride escape down the hollow handle.

The impact of the liquefied gas on the ebonite develops sufficient electricity to produce a continuous discharge of sparks 1 cm. long, between the metallic fittings of the ebonite tube and the connecting tube of the reservoir of the liquid. C. H. B.

## Inorganic Chemistry.

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**Apparatus for Preparing Oxygen Quickly.** By B. TACKE (*Ber.*, 17, 1831—1832).—This consists of a wrought-iron cylinder, 1 metre long and 4 cm. internal diameter, to the open end of which a flanged iron elbow delivery tube is screwed, the joint being made perfectly tight by the help of a leaden washer. The cylinder is filled with 700—800 grams of potassium chlorate, and laid horizontally, the end of the elbow tube (which points downwards) is then joined by means of a cork and mercury joint to a glass tube a metre long, and ending under mercury. The end of this tube is turned up under a funnel which contains a little caustic potash to wash the oxygen, and the funnel is connected with any convenient delivery tube. When as much oxygen as is required has been obtained, the source of heat is removed, and the mercury rises in the glass tube. The joints remain tight for any length of time, and the apparatus is ready for use again at a moment's notice. Should by any chance a leak take place, this is at once shown by the fall of the mercury in the glass tube.

L. T. T.

**Crystallisation of Sulphur.** By MAQUENNE (*Bull. Soc. Chim.*, 41, 238—239).—When hydrogen persulphide, either alone or mixed with carbon bisulphide, is allowed to decompose spontaneously, octahedral sulphur is deposited. If, however, the hydrogen persulphide is mixed with ether, the sulphur is deposited in perfectly transparent scales, which are extremely thin, and rapidly become opaque and transformed into a mass of octahedra, plainly visible under the microscope. When hydrogen persulphide is allowed to remain for 24 hours in the cold in contact with ether, decomposition takes place slowly, and orthorhombic crystals are formed, which often attain the length of from 8—10 mm. The yield is small; 500 grams of hydrogen persulphide gave only 4 grams of crystals perfect enough to examine. The crystalline form of the product, which was proved to be pure sulphur, was that of an orthorhombic prism, of  $106^{\circ} 20'$ , surmounted by an apex, the angles of which were identical with those of the ordinary octahedron. The faces *b* of the ordinary octahedron exactly form an angle of  $106^{\circ} 20'$ , and hence it would seem that this prism is a deformation of the octahedron, in which half the faces have been developed to the detriment of the others. The crystals melt at about  $117^{\circ}$ , and have a density of 2.041—2.049. They thus appear to be a variety intermediate between the  $\alpha$  and  $\beta$  varieties of crystallised sulphur. The crystals dissolve in carbon bisulphide and in benzene, and are deposited in octahedra when these solutions are evaporated. When immersed in superheated sulphur, or in a supersaturated solution, the crystals give rise to octahedra, which seem to be identical with those described by Gernez (*Abstr.*, 1884, 889), under the name of nacreous beads. It is probable that the crystals discovered by the author have previously been confounded with the clinorhombic



variety of sulphur, which they resemble in being readily transformed into the  $\alpha$ -form of the octahedron. W. R. D.

**Experiments to Combine Sulphur with Sulphur.** By H. PRINZ (*Annalen*, **223**, 371—378).—The author has tried a number of reactions in which it appeared probable that compounds would be formed containing sulphur in union with sulphur. In no case were such products formed. The reactions investigated were the following:—Sulphurous chloride and hydrogen sulphide do not react at ordinary temperatures; at  $60^\circ$  they yield hydrochloric acid, sulphur, and sulphurous anhydride. Sulphuric hydroxychloride and hydrogen sulphide react at ordinary temperatures, forming sulphuric acid, hydrochloric acid, sulphur sulphochloride, and sulphur. Ethyl sulphate and sulphur do not react at  $100^\circ$ . Ethyl sulphite and sulphur at  $200^\circ$  do not react, but the ethyl salt is decomposed. Ethyl sulphite and ethyl sulphide do not react at  $180^\circ$ . Sulphurous chloride and sodium mercaptide yield diethyl disulphide, sulphurous anhydride, hydrochloric acid, sodium chloride, sulphur, and carbon. Ethylsulphonic chloride and sodium mercaptide react at  $150^\circ$ , yielding sulphurous anhydride, hydrochloric acid, diethyl disulphide, sodium chloride, and carbon. Diethylic sulphoxide and sulphur do not react. A. J. G.

**Constitution of Disulphur Dichloride.** By H. PRINZ (*Annalen*, **223**, 355—371).—Carius having obtained disulphur dichloride,  $S_2Cl_2$ , by the action of phosphoric sulphide on sulphurous chloride, regarded its formation as being analogous to that of phosphoric sulphochloride from phosphoric sulphide and phosphoric oxychloride, and assigned to it the constitution  $S=S<\overset{Cl}{Cl}$  (sulphur sulphochloride). The author has reinvestigated the question with results that are, in his opinion, not in accord with Carius' theory.

*Experiments to convert Disulphur Dichloride into Sulphurous Chloride.*—Disulphur dichloride does not react with sulphurous anhydride even when heated with it for a day at  $100^\circ$ . It reacts with antimonious anhydride, or antimonie anhydride, forming antimonious chloride, sulphurous anhydride, and sulphur. With arsenious or arsenic anhydride, it yields arsenious chloride, sulphurous anhydride, and sulphur. It has no action on phosphorous or phosphoric anhydride. With selenious anhydride, it yields diselenium dichloride and sulphurous anhydride.

*Experiments to convert Sulphurous Chloride into Disulphur Dichloride.*—Sulphurous chloride when heated with sulphur for six hours at  $100^\circ$  is converted into disulphur dichloride and sulphurous anhydride. This, however, according to the author is not due to the replacement of oxygen by sulphur, but to the decomposition of sulphurous chloride into sulphurous anhydride and sulphur tetrachloride, the latter being then converted by the sulphur into disulphur dichloride. Sulphur has no appreciable action on phosphoric oxychloride, on acetic chloride or anhydride, on benzoic chloride, or on ethyl alcohol. Sulphurous chloride and antimony trisulphide react to form antimonious chloride, sulphur, and sulphurous anhydride. Sulphurous chloride when heated

with phosphoric sulphide for eight hours at  $100^{\circ}$  yields sulphurous anhydride, phosphoric sulphochloride, phosphoric oxychloride, and sulphur, not a trace of disulphur dichloride being formed. At  $150^{\circ}$ , disulphur dichloride is formed, but in all probability is due to the action of the liberated sulphur on sulphurous chloride. Selenium when heated for four hours at  $180^{\circ}$  with sulphurous chloride yields sulphurous anhydride, selenious chloride, and disulphur dichloride.

A. J. G.

**Compounds of Sulphurous Anhydride.** By A. GEUTHER (*Annalen*, **224**, 218—224).—The crystalline hydrate of sulphurous acid melts at  $14^{\circ}$ , and has the formula  $\text{SO}_2 \cdot 7\text{H}_2\text{O}$ , or  $\text{H}_2\text{SO}_3 \cdot 6\text{H}_2\text{O}$ .

*Potassium hydrogen sulphite*,  $\text{KHSO}_3$ , has an acid reaction. At  $190^{\circ}$ , it is decomposed into a mixture of sulphate and thiosulphate, and at a higher temperature sulphur sublimed and a polysulphide is produced.

*Potassium pyrosulphite*,  $\text{K}_2\text{S}_2\text{O}_5$ , behaves in a similar manner under the influence of heat.

The *neutral sulphite*,  $\text{K}_2\text{S}_2\text{O}_5 + 2\text{H}_2\text{O}$  is decomposed at a temperature below a red heat forming sulphate and polysulphide.

Ethoxythioxy chloride, which has been described by Michaelis and Wagner (*Ber.*, **7**, 1074), is decomposed on distillation into ethyl chloride and sulphurous anhydride.

W. C. W.

**Density of Sulphuric Acid.** By G. LUNGE (*Ber.*, **17**, 1748—1751). In answer to Mendelejeff (*Ber.*, Ref., 1884, 302), the author shows that the number 1.8384 obtained by him and Naef for the density of sulphuric acid at  $\frac{15^{\circ}}{4^{\circ}}$  is probably amongst the most correct, if not the most correct yet obtained, and does not "differ considerably" from Marignac's two determinations, but lies between them. He shows that the corrections applied by Mendelejeff to Marignac's earlier determination are not justifiable.

L. T. T.

**Compounds of Tellurous Anhydride with Acids.** By D. KLEIN (*Compt. rend.*, **99**, 326—328).—*Basic Tellurium Nitrate*,  $4\text{TeO}_2 \cdot \text{N}_2\text{O}_5 + 1\frac{1}{2}\text{H}_2\text{O}$ .—Tellurium is treated with a large excess of moderately strong nitric acid (sp. gr. 1.15—1.35), and the liquid evaporated at a gentle heat until crystals appear on the surface. As the liquid cools, crystals of the basic nitrate separate in considerable quantity. Basic tellurium nitrate is soluble in warm nitric acid diluted with five or six times its volume of water, and is deposited unchanged when the liquid cools. It begins to decompose at the melting point of lead, and the whole of the nitric acid is expelled at a dull red heat, a residue of tellurous anhydride being left. When this anhydride is dissolved in hot nitric acid, the basic nitrate is again formed.

*Basic tellurium sulphate*,  $2\text{TeO}_2 \cdot \text{SO}_3$ , is obtained by dissolving tellurous anhydride in hot sulphuric acid diluted with three or four times its weight of water, and evaporating the solution on a sand-bath. The basic sulphate is deposited in scales consisting of rhombic tables. It is only slightly soluble in cold dilute sulphuric acid.

Both the basic nitrate and the basic sulphate are decomposed by a large excess of warm water, a residue of tellurous anhydride being

left. The basic sulphate is probably the compound described by Berzelius as  $\text{TeO}_2, 2\text{SO}_3$ . C. H. B.

**Critical Temperature and Pressure of Nitrogen. Boiling Points of Nitrogen and Ethylene under Low Pressures.** By K. OLZEWSKI (*Compt. rend.*, 99, 133—136).—The following table gives the boiling point of ethylene under different pressures:—

Pressure.	Boiling point.	Pressure.	Boiling point.
750 mm.	— 103°	107 mm.	— 126°
546 "	— 105	72 "	— 129·7°
441 "	— 108	56 "	— 132°
346 "	— 111	31 "	— 139
246 "	— 115·5°	12 "	— 148
146 "	— 122°	9·8 "	— 150·4°

The critical temperature of nitrogen is — 146°, and the critical pressure 35 atmos. The following table shows the relation between the boiling point of liquid nitrogen and the pressure:—

Atmos.	Boiling point.
35	— 146°
31	— 148·2°
17	— 160·5
1	— 194·4
vacuum	— 213°

The author criticises some of Wroblewski's observations.

C. H. B.

**Critical Temperature and Pressure of Air; Relation between its Boiling Point and the Pressure.** By K. OLZEWSKI (*Compt. rend.*, 99, 184—186).—The air was liquefied under pressure in a glass tube cooled by means of ethylene. Its critical temperature is — 140°, and the critical pressure 39 atmos. The relation between the boiling point of liquid air and the pressure is shown in the following table:—

Pressure in atmos.	Boiling point.	Pressure in atmos.	Boiling point.
39·0	— 140°	12·5	— 160·5°
33·0	— 142	6·8	— 169·0
27·5	— 146	4·0	— 176·0
20·0	— 152	1·0	— 191·4
14·0	— 158·5°	vacuum	— 205·0

The boiling point of air under atmospheric pressure is practically that calculated from the boiling points of its constituents, but in a vacuum this relation does not hold good, and it would seem that the nitrogen evaporates more rapidly than the oxygen. C. H. B.

**Product of the Action of Bromine on Nitric Oxide.** By O. FROELICH (*Annalen*, 224, 270—273).—Landolt states that three com-

pounds,  $\text{NOBr}$ ,  $\text{NOBr}_2$ , and  $\text{NOBr}_3$  are formed by the action of bromine on nitric oxide. The author, however, regards the di- and tri-bromide as mixtures of nitrosyl bromide with free bromine, as they are completely separated into these constituents by distillation. When the so-called tribromide acts on sodium ethylate, a mixture of sodium bromide, sodium acetate, ethyl nitrite, and alcohol is obtained, showing that the body acts like a mixture of bromine and nitrosyl bromide.

W. C. W.

**Vitreous and Ordinary Amorphous Silica.** By D. LINDO (*Chem. News*, 50, 25—26).—According to text-books, silica, as obtained in the analysis of silicates, has the aspect of a white earthy powder. If the contents of the dish are stirred when crusts begin to form, and the stirring be continued until the mass is dry, the silica will always present this appearance to the unaided eye; under the microscope with reflected light, it will appear either in the form of amorphous dead-white masses, which in very thin layers are slightly translucent—ordinary amorphous silica; as a mass entirely composed of perfectly transparent particles with sharp edges and angles—vitreous silica; or, as a mixture of these two varieties. If the melt has been acted on by strong acid without dissolving it first in water, or if very little water has been used to dissolve it, the silica left on evaporating to dryness will be the ordinary amorphous form. If the melt has been dissolved in a considerable quantity of water, so that on adding the strong acid none of the silica is precipitated, all the silica will be in the vitreous form. If the melt has been dissolved in a moderate amount of water, so that on adding the acid part the silica is precipitated, and a portion held in solution, the silica will be found of both forms. If an acid solution of the melt in which all the silica remains dissolved is evaporated to dryness without stirring, the silica will form a transparent jelly, and on continuing to heat vitreous silica will be obtained in transparent particles, having the appearance, when washed and dried, of coarsely-powdered glass. It contains water, which can only be expelled completely by strong ignition. Ordinary amorphous silica examined in a drop of water under the microscope by transmitted light, will be found to consist of granular flakes, which have a yellowish-brown colour, whilst vitreous silica appears colourless. Ignited intensely over the blast it appears unaltered, and samples so treated retain their transparency after being exposed to the air for several weeks. Some samples retain their hygroscopic property after several intense ignitions; other samples lose this property completely after the first ignition. The author failed to detect any difference either in composition or appearance under the microscope in those samples that lost their hygroscopic property so readily, although he is inclined to attribute this peculiarity to the presence of foreign matter. Since Jenzsch has shown the existence of amorphous silica of sp. gr. 2.6, increase of density is no proof that the amorphous has passed into the crystalline state.

J. T.

**Phosphoric Anhydride.** By P. HAUTEFEUILLE and A. PERREY (*Compt. rend.*, 99, 33—35).—Phosphoric anhydride exists in three modifications, viz., crystalline, amorphous and pulverulent, amorphous

and vitreous. All three varieties are produced when phosphorus is burnt in a glass tube in a current of air, the crystalline form being deposited in the cold part of the tube, the pulverulent in the hotter part, and the vitreous in that part which is heated just to redness.

Crystallised phosphoric anhydride is obtained by distilling the products of the complete combustion of phosphorus. It forms colourless transparent highly refractive monoclinic crystals, which are either isolated or in snow-like masses, or in the form of an opaline crust, according to the conditions of condensation. At about  $250^{\circ}$ , the crystallised anhydride has a vapour-tension of 760 mm., but at a somewhat higher temperature it polymerises, and the vapour-tension sinks to a few mm. It can be rapidly distilled in a current of gas at  $250^{\circ}$ , but at a higher temperature distillation is much more difficult. It dissolves immediately in water, with development of 89.16 cal. for  $P_2O_5$ , forming a limpid solution.

Amorphous pulverulent phosphoric anhydride is a polymeride of the crystalline variety, and is obtained by heating the latter at  $440^{\circ}$ . It dissolves comparatively slowly in water, with development of 82.64 cal. for  $P_2O_5$ . The difference between this value and the heat of hydration of the crystalline variety, 6.52 cal., is the heat developed by polymerisation, and approaches closely to the heat of polymerisation of cyanuric acid (6.4 cal., Troost and Hautefeuille). The pulverulent anhydride is less volatile than the crystalline variety, and yields the latter when sublimed.

Vitreous phosphoric anhydride is obtained by heating either of the preceding varieties to incipient redness under pressure. It forms a colourless transparent glass which splits up, with phosphorescence, on cooling, owing to unequal contraction. It volatilises slowly but completely when heated to incipient redness, and yields the crystalline anhydride. The vitreous anhydride dissolves very slowly in water.

C. H. B.

**Phosphorus Sulphides.** By E. DERVIN (*Bull. Soc. Chim.*, **41**, 433—436).—When two parts of sulphur and one of phosphorus trisulphide ( $P_2S_3$ ) are dissolved in carbon bisulphide, and the solution exposed to the light for one or two months, fine pale-yellow transparent needles of the tetrasulphide,  $PS_4$ , are formed. This compound is not affected by heating under pressure with carbon bisulphide. In the above reaction crystalline spherical grains of  $P_4S_{11}(P_2S_3, 2PS_4)$  are also formed. This compound is produced more readily by heating in sealed tubes at  $180^{\circ}$  sulphur with phosphorus trisulphide, the latter in excess, dissolved in carbon bisulphide. When this compound is heated with carbon bisulphide under pressure at  $200^{\circ}$ , it is resolved into  $PS_4$  which crystallises out, and  $P_2S_3$  which remains dissolved. But this decomposition does not occur if a considerable quantity of the trisulphide is previously dissolved in the carbon bisulphide. Unsuccessful attempts were made by similar means to form compounds of the trisulphide with  $PS_3$  and  $PS_5$ . The pentasulphide,  $PS_5$ , was obtained by fusing sulphur with amorphous phosphorus, and was crystallised by heating under pressure with carbon bisulphide, but the compound  $PS_3$  could not be produced in a similar way; the fused mass yields crystals of  $PS_4$  when heated under pressure with carbon

bisulphide. The author considers that either the compound known as  $\text{PS}_3$  is a mixture of  $(\text{P}_2\text{S}_3, 2\text{PS}_4)$  with  $\text{PS}_4$ , or that the compound really exists in the fused mass, but is decomposed when heated with carbon bisulphide, yielding the tri- and tetra-sulphide  $5\text{PS}_3 = \text{P}_2\text{S}_3 + \text{PS}_4$ .

W. R. D.

**Polysulphides of Sodium.** By H. BÖTTGER (*Annalen*, 335—342).—*Sodium monosulphide*,  $\text{Na}_2\text{S} + 5\text{H}_2\text{O}$ , was prepared by saturating one-half of an alcoholic solution of soda with hydrogen sulphide, then adding the other half of the soda and allowing it to crystallise; access of air being carefully prevented. It forms long white prisms, loses 3 mol.  $\text{H}_2\text{O}$  at  $100^\circ$ , is rendered anhydrous by heating to  $180^\circ$ , and oxidises readily on exposure to air. The hydrated salt is readily and completely decomposed by carbonic anhydride in the cold, whilst the anhydrous salt is only appreciably decomposed on heating above  $100^\circ$  in a current of the gas.

The polysulphides were prepared by heating on the water-bath alcoholic solutions of the monosulphide with the calculated amount of sulphur, the liquid being subsequently cooled to  $-10^\circ$  to  $-15^\circ$  to obtain crystals.

*Sodium disulphide*,  $\text{Na}_2\text{S}_2 + 5\text{H}_2\text{O}$ , forms groups of sulphur-yellow crystals. It loses 3 mols.  $\text{H}_2\text{O}$  at  $100^\circ$ .

*Sodium trisulphide*,  $\text{Na}_2\text{S}_3 + 3\text{H}_2\text{O}$ , forms dark golden-yellow concentrically grouped crystals. It loses 2 mols.  $\text{H}_2\text{O}$  at  $100^\circ$ , fusing to a liver-coloured mass, and becomes anhydrous at  $190^\circ$ .

*Sodium tetrasulphide*,  $\text{Na}_2\text{S}_4 + 8\text{H}_2\text{O}$ , is obtained in orange-red, concentrically grouped crystals. Heated above  $100^\circ$ , a part of its sulphur is evolved as hydrogen sulphide.

*Sodium pentasulphide*,  $\text{Na}_2\text{S}_5 + 8\text{H}_2\text{O}$ , forms dark orange-yellow crystals. It commences to decompose at  $100^\circ$ .

A. J. G.

**Constitution of the Alkali Polysulphides.** By H. BÖTTGER (*Annalen*, 223, 342—345).—If the alkali tetra- and penta-sulphides are the analogues of the sulphites and sulphates, containing sulphur in place of oxygen, they should, in the author's opinion, on being boiled with lead hydroxide, yield plumbic sulphide, and the alkaline sulphite or sulphate respectively. On boiling a solution of sodium pentasulphide with lead hydroxide, the products obtained were lead sulphide and sodium thiosulphate. Sodium tetrasulphide yields the same products, and, in addition, sodium hydroxide.

A. J. G.

**Constitution of Polysulphides and Polyoxides.** By A. GEUTHER (*Annalen*, 224, 201—218).—The author is of opinion that the constitution of the polysulphides and polyoxides can only be explained on the assumption of the variable valency of the elements. He fixes the maximum valency of potassium and sodium at 5, and of barium, strontium, and calcium at 10.

W. C. W.

**Relation between the Pressure and the Temperature of Transformation of Silver Iodide.** By MALLARD and LE CHATELIER (*Compt. rend.*, 99, 157—160).—Silver iodide changes at  $146^\circ$  from the hexagonal to the cubic system (this vol., p. 16), with absorption

of heat and contraction of volume. The phenomenon is analogous to the freezing of water, and it might be expected that an increase of pressure would lower the temperature of transformation, and that under very high pressure the transformation would take place at the ordinary temperature. By means of a screw press provided with a Bourdon manometer similar to that used in their experiments on combustion, the authors find that the transformation of silver iodide takes place at the ordinary temperature under somewhat high pressure, and when the pressure is released the iodide returns to its original condition. At  $20^{\circ}$  the pressure required to effect the change is about 2475 kilos. per square centimetre, and under this and all higher pressures the silver iodide crystallises in the cubic system, whilst under lower pressures it crystallises in the hexagonal system.

The change under pressure is accompanied by a contraction of 0.16, a contraction about ten times as great as that observed by Rodwell at  $146^{\circ}$  under atmospheric pressure; approximate determinations by the authors indicate that the contraction at  $146^{\circ}$  is about 0.11. C. H. B.

**Ammonio-silver Compounds.** By A. REYCHLER (*Ber.*, 17, 1840—1842).—Dry silver phosphate,  $\text{Ag}_3\text{PO}_4$ , was kept for some time in an atmosphere of ammonia. At the end of 14 days absorption had almost entirely ceased, and 1 mol. of phosphate had then absorbed between 3 and 4 mols.  $\text{NH}_3$ . As the silver compound always shows a slight tint of yellow, the author believes the pure compound to have the formula  $\text{Ag}_3\text{PO}_4 \cdot 4\text{NH}_3$ . By the action of ethyl iodide on ammonio-silver nitrite, nitroethane is formed besides the compounds already mentioned (this vol., 157). With methyl iodide the reaction is quite analogous to that with ethyl iodide, ammonia, silver iodide, methyl nitrite and nitromethane being produced. L. T. T.

**Crystallised Barium Manganite.** By G. ROUSSEAU and A. SAGLIER (*Compt. rend.*, 99, 139—141).—A mixture of 2 grams barium manganate and 10 grams barium chloride was heated in a platinum crucible in a Forquignon and Leclercq furnace at  $1500$ — $1600^{\circ}$  for four hours, allowed to cool, and the fused mass treated several times with boiling water to remove chloride and undecomposed manganate, and finally with dilute acid to remove a small quantity of carbonate. The residue consisted of small opaque bluish-black crystals, with a lustre resembling that of crystallised silicon; sp. gr. = 5.85. These crystals have the composition  $\text{BaMnO}_3$ , and dissolve readily in hydrochloric acid with evolution of chlorine, but are not so soluble in nitric acid. This crystallised barium manganite is quite distinct from psilomelane, and its existence affords further evidence that manganese peroxide is really an acid-forming oxide. C. H. B.

**Compounds of Haloid Salts with Oxysalts of the same Metal.** By H. LE CHATELIER (*Compt. rend.*, 99, 276—279).—When a mixture of boric anhydride and calcium oxide in any proportions is thrown into fused calcium chloride, the mixture becomes incandescent

and dissolves completely to a clear liquid, but after some time the liquid becomes turbid owing to the separation of a crystalline *calcium chloroborate*, which can be obtained, by gradual solidification, in triclinic prisms several millimetres in length. This compound has the composition  $3\text{CaO}, \text{B}_2\text{O}_3, \text{CaCl}_2$ . It is slowly decomposed by alcohol and rapidly by water or moist air.

*Calcium chloroferrite*,  $2\text{CaO}, 2\text{Fe}_2\text{O}_3, \text{CaCl}_2$ , is obtained in a similar manner, and forms very brilliant prisms with easy cleavage, the angle between the faces of the prism being  $139^\circ$ . This compound is usually obtained in thin lamellæ which are not altered by water or air.

Similar experiments with sulphuric and carbonic acids, chromium, aluminium, and zinc oxides, and manganese peroxide gave negative results.

C. H. B.

**Calcium Oxychloride, Silicates, and Chlorosilicates: Artificial Production of Wollastonite.** By A. GORGEU (*Compt. rend.*, 99, 256—259).—When calcium chloride is fused at a bright red heat in a current of moist air, it is gradually converted into oxychloride and eventually into oxide. The oxychloride appears to have the composition  $\text{CaCl}_2, \text{CaO}$ , but cannot be isolated because it is rapidly decomposed by alcohol and water. As the fused mass approaches this composition, the evolution of hydrochloric acid slackens considerably, but never ceases entirely until the whole mass is converted into oxide. If fusion is stopped at this point and the broken residue is left in contact with strong alcohol for two days, it yields insoluble slender needles, or birefractive lamellæ, which contain only 1 mol. calcium chloride to 8 mols. of calcium oxide, and are soluble in a solution of sugar. The presence of silica facilitates the decomposition of the chloride, but the presence of alkaline chlorides retards it considerably.

The action of precipitated silica on calcium chloride, in equal molecular proportions, at a high temperature, in presence of water-vapour, yields the silicate  $\text{CaSiO}_3$ , whilst with twice the amount of chloride the normal silicate  $\text{Ca}_2\text{SiO}_4$  is formed. If the proportion of chloride is as high as 7 mols., chlorosilicates alone are obtained, and in presence of 20 per cent. of an alkaline chloride, the product is identical with wollastonite. With finely powdered sand in place of precipitated silica, decomposition takes place more slowly.

One of the chlorosilicates obtained,  $\text{SiO}_2, 2\text{CaO}, \text{CaCl}_2$ , has been described by Le Chatelier (*Compt. rend.*, 1883). It forms rectangular birefractive plates belonging to the rhombic system. The other seems to have the composition  $\text{SiO}_2, \text{CaO}, \text{CaCl}_2$ , and forms almost regular hexagonal plates, the two optical axes of which approach each other very closely. The formation of the first compound requires prolonged fusion in presence of moisture, whilst the second is formed much more rapidly. Both compounds are decomposed by water and a solution of carbonic acid, and dissolve easily in dilute acids, although the acid silicate is insoluble in a 5 per cent. solution of acetic acid.

Artificial wollastonite is obtained by fusing 1 gram of silica with 15 grams of calcium chloride and 3 grams of common salt at a cherry-



red heat in a current of moist air for half an hour. The product is treated with cold water and acetic acid, and a residue is obtained consisting of long prisms of wollastonite mixed with round grains of tridymite. Artificial wollastonite is identical in chemical and optical properties and crystalline form with the natural mineral, but is somewhat softer, the hardness of the mineral being 5, whilst that of the artificial product is only 3·5.

C. H. B.

**Calcium Oxysulphides.** By A. GEUTHER (*Annalen*, **224**, 178—201).—The crystals which Herschell obtained by boiling sulphur in milk of lime and allowing the solution to cool in a vessel from which air was excluded, have been analysed by Rose, Schöne (*Pogg. Ann.*, **117**, 17) and others. They have the composition  $\text{CaS}_3 \cdot 2\text{CaO} + 10$  or  $11\text{H}_2\text{O}$ . The crystals dissolve in hydrochloric acid with formation of hydrogen supersulphide,  $\text{H}_2\text{S}_3$ , and a slight evolution of sulphuretted hydrogen. Schöne regarded the compound as  $\text{CaS}_3 \cdot 3\text{CaO} + 12\text{H}_2\text{O}$ , but his results are vitiated by the fact that he decomposed the crystals before analysis by washing them with water.

Buchner's crystals, prepared by acting on milk of lime with sulphuretted hydrogen and slightly exposing the solution to the atmosphere, or by boiling calcium monosulphide with water and sulphur, have also been investigated by Rose and by Schöne. The former assigns to the compound the formula  $\text{CaS}_3 \cdot 5\text{CaO} + 20\text{H}_2\text{O}$ , while the latter regards it as  $\text{CaS}_4 \cdot 4\text{CaO} + 18\text{H}_2\text{O}$ . The author considers that the composition of the crystals is best represented by  $\text{CaS}_3 \cdot 3\text{CaO} + 14$  or  $15\text{H}_2\text{O}$  (compare Divers, *Trans.*, 1884, p. 270). The existence of the strontium oxysulphide,  $\text{SrS}_4 \cdot \text{SrO} + 12\text{H}_2\text{O}$ , described by Schöne, is regarded by the author as doubtful.

W. C. W.

**Preparation of Di- and Tri-calcium Phosphates by Precipitation.** By E. L. DE BOUQUET (*Bied. Centr.*, 1884, 411).—The process is the subject of a patent. Into a hydrochloric acid solution of a phosphate is run, in fine jets, a solution of calcium hydrosulphide, preferably obtained from the residues of the Leblanc soda process. Sulphuretted hydrogen escapes, and the diphosphate is precipitated; if the acid solution is treated with the reagent to complete alkaline reaction, the triphosphate is reformed.

J. F.

**Crystallised Aluminium Orthophosphate.** By A. DE SCHULTEN (*Compt. rend.* **98**, 1583—1584).—A concentrated solution of sodium aluminate is strongly acidified with phosphoric acid and heated in sealed tubes at  $250^\circ$  for several hours. Aluminium orthophosphate  $\text{Al}_2(\text{PO}_4)_3$ , is deposited in small pointed hexagonal prisms of sp. gr. about 2·59. The crystals do not lose weight at a bright red heat, and do not melt even at a white heat. They are insoluble in concentrated nitric and hydrochloric acids and are attacked with difficulty by hot concentrated sulphuric acid, but they are decomposed when fused with sodium carbonate.

The presence of sodium phosphate seems to be essential to the crystallisation of aluminium phosphate. If aluminium hydroxide or aluminium chloride is heated with phosphoric acid in a sealed tube,

only a fine crystalline powder is obtained, but if the phosphoric acid is replaced by a very acid solution of sodium phosphate, the aluminium phosphate is obtained in distinct prisms.

By varying the proportions of the reagents, crystallised double phosphates may be obtained. Arsenic acid yields similar derivatives.

C. H. B.

**Some Fluorine Compounds of Copper.** By L. BALBIANO (*Gazzetta*, 14, 74—84).—The compounds formed by the action of ammonia on cupric chloride, bromide, and iodide have been prepared and examined, but as the corresponding fluorine derivatives are unknown, the author thought it desirable to undertake their investigation.

*Copper Fluorides.*—A fluoride and an oxyfluoride of copper were described by Berzelius, but no analysis of the latter was made. The author endeavoured to prepare cupric fluoride, by mixing warm solutions of cupric sulphate and potassium fluoride, but found that a greenish-white precipitate of cupric oxyfluoride,  $\text{CuF.OH}$ , was at once formed, whilst potassium cupric sulphate remained in solution, and was deposited as the solution cooled, the reaction being  $2\text{CuSO}_4 + 2\text{KF} + \text{H}_2\text{O} = \text{CuF.OH} + \text{CuK}_2(\text{SO}_4)_2 + \text{HF}$ . Similar results were obtained with cupric chloride except that no double potassium salt was formed.

The oxyfluoride is formed with great readiness, for when cupric oxide or carbonate is added to solution of hydrofluoric acid, the oxyfluoride begins to separate long before the acid is saturated. In order to prepare cupric fluoride, cupric carbonate is dissolved in aqueous hydrofluoric acid, and alcohol of 95 per cent. added, when the fluoride,  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ , is precipitated as a pale blue crystalline powder which is only sparingly soluble in water and is very readily decomposed, with formation of the oxyfluoride. This happens if the solution is heated; the crystals decompose also in 4 or 5 days with evolution of hydrofluoric acid if kept in a glass bottle, and more slowly in a platinum vessel. Cupric fluoride absorbs ammonia readily in accordance with the requirements of the equation  $\text{CuF}_2 \cdot 2\text{H}_2\text{O} + 3\text{NH}_3 = \text{CuOHf}(\text{NH}_2)_2 + \text{NH}_4\text{F} + \text{H}_2\text{O}$ , yielding a product soluble in water; all attempts, however, to isolate a cuprammonium compound were ineffectual, the oxyfluoride being invariably obtained instead.

*Cupric Fluosilicate.*—This salt was prepared by Stolba's method (*J. pr. Chem.* 102, 7) and twice recrystallised. It contains 6 mols.  $\text{H}_2\text{O}$  (Marignac 6; Stolba  $6\frac{1}{2}$ ), two of which it loses at  $90^\circ$ , or in a vacuum over sulphuric acid. When heated to  $130$ — $140^\circ$ , it is decomposed in accordance with the equation  $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O} = \text{CuF.OH} + \text{SiF}_4 + \text{HF} + 5\text{H}_2\text{O}$ , a residue of cupric oxyfluoride being left. Cupric fluosilicate containing 4 mols.  $\text{H}_2\text{O}$ , absorbs ammonia, but no cuprammonium derivative of hydrofluosilicic acid is formed. On treating the bright blue product of the reaction with water, a blue mass is left undissolved, consisting of silica and a cuprammonium compound; the latter is soluble in dilute ammonia, and on heating this solution cupric oxyfluoride is deposited. The action of ammonia on the fluosilicate is therefore:  $\text{CuSiF}_6 \cdot 4\text{H}_2\text{O} + 7\text{NH}_3 = \text{CuF.OH} \cdot 2\text{NH}_3 + 5\text{NH}_4\text{F} + \text{SiO}_2 + \text{H}_2\text{O}$ .

The water of crystallisation in the fluorine compounds of copper seems to have great influence on the action of ammonia. It is possible, however, that cuprammonium compounds might be formed from the anhydrous fluorides by the action of ammonia.

C. E. G.

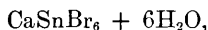
**Bromine Compounds of Tin.** By B. RAYMAN and K. PREIS (*Annalen*, **223**, 323—334).—Most of the results detailed in this paper have already appeared (Abstr., 1883, 424), the following are new:—

*Stannous bromide*,  $\text{SnBr}_2$ , prepared according to Baland's method, by heating tin in a current of hydrobromic acid, and purified by distillation, forms a transparent crystalline mass of pale-yellow colour, melts at  $215.5^\circ$  to a pale-yellow transparent liquid, and resolidifies at  $215^\circ$ . It has sp. gr. 5.117 at  $17^\circ$ . Water partly decomposes it with separation of a white oxybromide.

A *hydrate of stannous bromide*,  $\text{SnBr}_2 + \text{H}_2\text{O}$ , is obtained by dissolving tin in warm concentrated hydrobromic acid. It can be obtained crystallised in colourless needles or in thin prisms. *Ammonium stannous bromide*,  $(\text{NH}_4)_2\text{SnBr}_4 + \text{H}_2\text{O}$ , forms fine colourless needles. *Ammonium stannous chlorobromide*,  $(\text{NH}_4)_2\text{SnBr}_2\text{Cl}_2 + \text{H}_2\text{O}$ , is obtained by strongly cooling mixed solutions of stannous bromide and ammonium chloride. It forms white porcelain-like crystals of the rhombic system,  $a : b : c = 0.69588 : 1 : 0.77240$ . Observed faces  $\infty\text{P}$ ,  $\infty\text{P}\infty$ ,  $\text{P}\infty$ . Crystals were also obtained containing less chlorine than the above.

*Stannic bromide* is obtained by sublimation in small well-formed crystals showing numerous faces and possessing almost the lustre of the diamond. The following double salts are described; they are obtained by evaporation and crystallisation of mixed solutions of the component salts:—

*Sodium stannic bromide*,  $\text{Na}_2\text{SnBr}_6 + 6\text{H}_2\text{O}$ , forms pale-yellow prismatic crystals, very soluble in water. *Calcium stannic bromide*,



crystallises in slender needles and is very deliquescent. *Strontium stannic bromide*,  $\text{SrSnBr}_6 + 6\text{H}_2\text{O}$ , could only be obtained mixed with stannic bromide as a pale-yellow, deliquescent, crystalline mass. *Magnesium stannic bromide*,  $\text{MgSnBr}_6 + 10\text{H}_2\text{O}$ , forms deliquescent pale-yellow tabular crystals. *Manganous stannic bromide*,  $\text{MnSnBr}_6 + 6\text{H}_2\text{O}$ , forms large pale-yellow deliquescent crystals. *Ferrous stannic bromide*,  $\text{FeSnBr}_6 + 6\text{H}_2\text{O}$ , forms granular crystals of green to yellow colour. *Nickel stannic bromide*,  $\text{NiSnBr}_6 + 8\text{H}_2\text{O}$ , forms apple-green granular deliquescent crystals. *Cobalt stannic bromide*,  $\text{CoSnBr}_6 + 10\text{H}_2\text{O}$ , is obtained in yellowish-red tabular deliquescent crystals.

A. J. G.

**Idunium, a New Element.** By M. WEBSKY (*Dingl. polyt. J.*, **253**, 391).—The author found an element resembling vanadium in a mineral obtained from the Aquadita Mine, La Plata. This mineral was composed mainly of zinciferous lead vanadate. On treating the vanadic acid with ammonium chloride, ammonium vanadate is pre-

precipitated, idunic acid remaining in the mother-liquor, which on addition of ammonium sulphide is separated as red idunic oxide.

D. B.

**Arsenovanadic Acid.** By P. FERNANDEZ (*Ber.*, **17**, 1632).—Chemically pure vanadic acid, obtained by precipitating ammonium metavanadate with nitric acid, is added in excess to a warm concentrated solution of arsenic acid, and the whole boiled for some hours. The solution is then filtered and concentrated, when brilliant gold-coloured crystalline nodules are obtained. The arsenovanadic acid thus formed has the composition  $\text{As}_2\text{O}_5, \text{V}_2\text{O}_5, 11\text{H}_2\text{O}$ .

A. K. M.

**New Tungstoborates.** By D. KLEIN (*Compt. rend.*, **99**, 35—37).—When 3 parts of boric acid are dissolved in a boiling solution of 4 parts of sodium paratungstate, the liquid yields no precipitate with inorganic acids. The excess of boric acid and the borates which are formed are removed by crystallisation, when a heavy mother-liquor is obtained closely resembling that produced by the action of boric acid on normal sodium tungstate (*Abstr.*, 1881, 224, and *Compt. rend.* **91**, 1070). When this mother-liquor is evaporated over sulphuric acid, it deposits the disodium tungstoborate previously described. If the still liquid portion is acidified with hydrochloric acid and mixed with barium chloride, it yields a pulverulent white precipitate, and the filtrate on concentration deposits rhombohedral crystals which are under examination, and afterwards triclinic prisms, which when recrystallised yield a salt crystallising in quadratic octahedra—in all probability di-barium tungstoborate (*loc. cit.*). The triclinic salt has the composition  $10\text{WO}_3, \text{B}_2\text{O}_3, 2\text{BaO} + 16\text{H}_2\text{O}$ .

If the mother liquor from the sodium tungstoborate is concentrated without addition of hydrochloric acid, it yields first a pulverulent deposit and afterwards monoclinic crystals which have the same composition as the triclinic crystals already described, and like them are decomposed by recrystallisation.

C. H. B.

**Double Chlorides of Chromium.** By L. GODEFROY (*Compt. rend.*, **99**, 141—144).—The amorphous violet substance obtained when an excess of hydrochloric acid acts on potassium dichromate in presence of a little alcohol is not pure chromic potassium chloride, but is a mixture of this salt with chromic chloride. Compounds of chromic chloride with other metallic chlorides are formed whenever the two chlorides are brought in contact in presence of hydrochloric acid of at least 32.5 per cent. Combination is promoted by elevation of temperature, but is prevented within certain limits by the presence of water. The best method, however, of preparing the chromic potassium chloride,  $\text{Cr}_2\text{Cl}_6, 4\text{KCl}$ , for example, is to mix 700 grams of alcohol with 300 grams of finely powdered potassium dichromate, and pass chlorine gas into the mixture for six or eight hours. The theoretical yield of the double chloride is obtained as a violet-red precipitate.

The double chlorides obtained by this method form crystalline powders of various colours, the colour deepening and varying in tint

with elevation of temperature. They can be obtained in distinct crystals by heating the powders with a sufficient quantity of 40 per cent. hydrochloric acid in sealed tubes at  $120-130^{\circ}$ , and cooling very slowly. The double chlorides are very stable even at a high temperature, but they decompose rapidly in presence of a trace of moisture. When thrown into water, they at first dissolve with their characteristic colour, but the double salt quickly decomposes with formation of hydrochloric acid, the chloride of the second metal, and an oxychloride which crystallises with difficulty. Decomposition ceases when the liquid contains 32.5 per cent. of free hydrochloric acid.

Double iodides and bromides are obtained under the same conditions.

C. H. B.

**Chromic Acid and Chromic Anhydride.** By H. MOISSAN (*Compt. rend.*, **98**, 1581—1583).—*Purification of Chromic Anhydride.*—In order to purify chromic anhydride from sulphuric acid, which it frequently contains, it is very carefully fused in a platinum capsule, heated until the greater part of the sulphuric acid is driven off, and the contents of the capsule then poured on to a porcelain slab. The unexpelled sulphuric acid runs out first, and the chromic anhydride which afterwards flows from the capsule and solidifies almost instantly contains but traces of sulphuric acid.

*Chromic Acid.*—An excess of chromic anhydride is mixed with a small quantity of water, the mixture heated at  $100^{\circ}$  for a short time, and the liquid poured off and cooled in melting ice. After some time, it deposits small red highly deliquescent crystals which melt readily, and give off water when heated, leaving chromic anhydride. The crystals have the composition  $\text{H}_2\text{CrO}_4$ .

*Action of Hydrochloric Acid Gas on Chromic Anhydride.*—When purified and dry chromic anhydride is treated with hydrochloric acid gas, chromyl dichloride is formed at ordinary temperatures, and the reaction is accelerated by heat. The water which is also produced decomposes part of the chromyl dichloride, and yields an oily substance entirely soluble in water. This substance was obtained by Dumas, but has not been analysed. Hydrobromic and hydriodic acids under the same conditions give no similar reaction. Perfectly dry chlorine has no action on chromic anhydride, but if it contains hydrochloric acid, or if it contains water and is heated at  $150^{\circ}$ , chromyl dichloride is formed.

The chromates of the alkalis, barium, lead, and silver all yield chromyl dichloride when treated with hydrochloric acid gas.

C. H. B.

**Sulphur Compounds of Molybdenum.** By G. KRÜSS (*Ber.*, **17**, 1769—1774).—In a previous communication (this vol., 160) the author described, under the name of orthoxythiomolybdates, a series of salts derived from an acid,  $\text{H}_2\text{MoO}_2\text{S}_2$ , lying midway between  $\text{H}_2\text{MoO}_4$  and  $\text{H}_2\text{MoS}_4$ . He has now obtained other intermediate acids, and therefore proposes to modify his nomenclature by calling the above compounds dithiomolybdates. The following table contains the new compounds he has obtained :—

Name.	Formula.	Character.	Behaviour with water.
Sodium monothiomolybdate..	$\text{Na}_2\text{MoO}_3\text{S}$	Pale yellow crystalline	Soluble to golden solution.
Potassium dithiomolybdate ..	$\text{K}_2\text{MoO}_2\text{S}_2$	Golden yellow needles	Soluble.
Potassium sulphomolybdate..	$\text{K}_3\text{Mo}_4\text{S}_9\text{O}_7$	Yellow monoclinic prisms	Soluble.
Perthiomolybdic acid .....	$\text{H}_2\text{MoS}_5$	Red, amorphous	Very sparingly soluble.
Hydrogen potassium perthiomolybdate	$\text{KHMoS}_5$	Red, crystalline	—

The three first-named salts were obtained by melting together molybdic acid and the respective alkaline carbonate, and treatment of the melt with alkaline sulphide. The free acid may be obtained from the last salt in the above list by treating it with acetic acid. Potassium sulphide dissolves this acid to a brownish-red solution, which probably contains  $\text{K}_2\text{MoS}_5$ . This salt is, however, very unstable, and its solution is decomposed by boiling with evolution of hydrogen sulphide, separation of sulphur, and formation of molybdenum trisulphide.

L. T. T.

**Sulphur Compounds of Molybdenum.** By G. KRÜSS (*Annalen*, 225, 1—57).—In this paper a fuller account is given of the preparation and properties of sulphur compounds of molybdenum described by the author in the *Berichte* (this vol., p. 160, and preceding Abstract). The principal classes of compounds here investigated are the oxythiomolybdates, the thiomolybdates, and the perthiomolybdates.

*Oxythiomolybdates*, intermediate between the molybdates and the thiomolybdates, are divisible into several series according as the oxygen-atoms of molybdic acid are replaced by sulphur. *Monothiomolybdates* of general formula  $\text{M}'_2\text{MoO}_3\text{S}$ , in which  $\text{M}'$  represents a monatomic metal. The sodium salt obtained by treating sodium trimolybdate with sodium hydrogen sulphide is a hygroscopic golden substance, a solution of which gives a blue coloration with sulphuric acid, probably due to the liberation of monothiomolybdic acid. *Dithiomolybdates* of general formula  $\text{M}'_2\text{MoO}_2\text{S}_2$ , obtained by passing hydrogen sulphide into concentrated solutions of the molybdates in the alkaline hydrates, crystallise in golden or reddish-golden needles. Derivable from them are the *pyrodithiomolybdates* of general formula  $\text{M}'\text{HMo}_2\text{O}_4\text{S}_3$ , the salts of an acid,  $\text{H}_2\text{Mo}_2\text{O}_4\text{S}_3$  ( $2\text{H}_2\text{Mo}_2\text{O}_4\text{S}_2 - \text{H}_2\text{S}$ ), which stand in the same relation to dithiomolybdates as ortho- to pyro-phosphoric acid,\* the ammonium salt of which, on treatment with ammonia, is reconverted into the ammonium salt of dithio-

\* In the Abstract mentioned, the last two lines on p. 160 should read thus: Ammonium pyroxythiomolybdate is a reddish golden precipitate, having the composition  $\text{NH}_4\cdot\text{HMo}_2\text{O}_4\text{S}_3$ , the salt of an acid,  $\text{H}_2\text{Mo}_2\text{O}_4\text{S}_2$  ( $= 2\text{H}_2\text{MoO}_2\text{S}_2 - \text{H}_2\text{S}$ ), &c.

molybdc acid, thus:  $\text{NH}_4\text{HMo}_2\text{O}_4\text{S}_3 + \text{NH}_3 = (\text{NH}_4)_2\text{MoO}_2\text{S}_2 + \text{MoO}_2\text{S}$ . Solutions of the alkali pyromolybdates give brown or reddish-brown precipitates with solutions of salts of aluminium, chromium, manganese, copper, lead, silver, and uranium; and yellow precipitates with mercury, platinum, lanthanum, and caesium salts. There is also described a potassium thiomolybdate,  $\text{K}_8\text{Mo}_4\text{S}_9\text{O}_7$ , prepared by dissolving potassium trimolybdate in potassium hydrosulphide, with addition of alcohol. A red oil is precipitated, from which golden-yellow monoclinic prisms can be separated. This salt can be distinguished from potassium thio- and dithio-molybdate by forming an immediate precipitate with solutions of barium salts.

*Thiomolybdates*,  $\text{M}_2\text{MoS}_4$ , obtained by passing hydrogen sulphide into solutions of the molybdates in concentrated alkalis, are brilliant red compounds, crystallising in the rhombic system. If the alkalis be more concentrated, salts are formed of the composition  $\text{M}_6\text{Mo}_2\text{S}_9$ , called *basic thiomolybdates*, of which the potassium salt crystallises in red rectangular plates. Its aqueous solution gives yellow precipitates with calcium, strontium, and magnesium salts, golden-brown with manganese, and olive-green with cadmium salts.

The oxythio- and thio-molybdates give a golden-green coloration to a Bunsen flame; the absorption spectrum of aqueous solutions of the oxythiomolybdates is at the most refrangible end of the spectrum, but of the normal thiomolybdates at the red end.

*Perthiomolybdates*.—In the course of the preparation of molybdenum tetrasulphide, there was obtained a certain quantity of blood-red crystals of the composition  $\text{KHMoS}_5$ , probably formed by the action of hydrogen sulphide on potassium pyrothiomolybdate, an intermediate product of the reaction, thus:  $\text{K}_2\text{Mo}_2\text{O}_7 + \text{H}_2\text{S} = \text{KHMoS}_5 + \text{KHS} + \text{MoS}_2$ . In solutions of this salt, dilute acids cause a precipitation of perthiomolybdc acid,  $\text{H}_2\text{MoS}_5$ , insoluble in water and alcohol. It readily gives off hydrogen sulphide, and is converted into molybdenum tetrasulphide. This potassium salt forms the first case of an acid primary thio-salt; it may be reproduced from the acid by heating it with potassium hydrosulphide.

In conclusion, brief mention is made of sulphur-derivatives of vanadic and manganic acids.

V. H. V.

## Mineralogical Chemistry.

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**Presence of the Diamond in an Indian Pegmatite.** By CHAPER (*Ann. Chim. Phys.* [6], 2, 284—288).—After noticing the various theories as to the origin and formation of the diamond, the author announces that he has found diamonds *in situ* in a pegmatite, in Nizam, in the Presidency of Madras. The results of his observations show that the pegmatite contains epidote to a large amount, and also oligoclase and microcline, and it seems more than probable that it is this rock which has furnished the diamonds contained in the



various deposits worked in Hindostan. There appears to be more than one mode of formation of the diamond, as it would be very difficult to show any analogy between the pegmatite and either the magnesian mud of the South African diamond beds, or the rock which has given rise to the latter by its disintegration, as it contains no granitic fragments.

As the diamond has been found in a rock as ancient as pegmatite, it may be found in all the products of the erosion or disintegration of pegmatite; that is to say, in the quartzites with or without mica, in the clays, in pudding-stones, &c. Moreover, the presence of the diamond in itacolumites and other secondary rocks, accompanied by crystallised quartz, apatite, rutile, oligist, &c., is no evidence that it has been formed in the sedimentary deposits.

C. E. G.

**Origin and Distribution of Phosphorus in Coal and Cannel Coal.** By A. CARNOT (*Compt. rend.*, 99, 154—156).—The presence of phosphorus in coal ash has already been observed by several chemists. The author has determined the amount of this element in various fossil plants, and in different samples of coal, with the following results:—

	P per cent.	
	I.	II.
Fossil calamodendrom .....	0·00195	0·00245
„ cordaites .....	0·00082	traces
„ lepidodendron .....	traces	traces
„ psaronius (fern) .....	0·00271	0·00712
Mineral charcoal .....	0·00399	
Coal from Commentry .....	0·00163	
„ Ferrières .....	0·01385	
Anthracite .....	0·01467	
Cannel from Commentry .....	0·04260	0·03912
„ Lancashire .....	0·02852	
„ Wigan .....	0·02246	
„ Newcastle ..	traces	
„ Glasgow .....	0·00572	
„ Virginia .....	0·02771	
Paraffin shale from New South Wales .....	0·01956	
Boghead cannel from Autun ....	traces	
„ „ Frioul ....	0·06275	

Microscopic examination shows that cannel is composed of decomposed vegetable fragments of very various character, but generally contains a large number of spores or pollen grains very irregularly distributed (Renault). The two specimens which were almost free from phosphorus were found to be equally free from spores. Analysis of the spores and pollen of the modern representatives of carboniferous plants (*Lastræa*, *Polystichum*, *Osmunda*, *Lycopodium*, &c.) shows that these parts are very much richer in phosphorus than the other organs of the plants. It follows that the greater part of the

phosphorus present in coal has been derived from the spores and the pollen of the plants from which it has been formed.

In the same piece of coal, there are frequently alternate brilliant and dull layers, the former having been derived from the wood, bark, and roots, the latter from the leaves and other *débris*. In a sample from Commentry the dull layers gave 10·5 per cent. of ash, and contained 0·00815 per cent. of phosphorus; the bright layers contained 3·8 per cent. of ash and 0·00326 of phosphorus. C. H. B.

**Deposit of Saltpetre (Potassium Nitrate) at Cochabamba, Bolivia.** By SACC (*Compt. rend.*, 99, 84—85).—To the east of Cochabamba, near the village of Arané, there is an immense saline deposit of the composition: Potassium nitrate, 60·7; borax, traces of sodium chloride and water, 30·7; organic matter, 8·6 = 100. The soil on which this deposit rests is brown and inodorous when dry, but when moistened it evolves ammonium carbonate and hydrosulphide. It has the composition:—incombustible residue, 74·2; borax and salts, 15·5; organic matter, water, and ammonium salts, 10·3 = 100. The incombustible residue consists of very fine sand, and a very large proportion of calcium, iron, and magnesium phosphates. The saltpetre has been formed by the oxidation of the ammoniacal salts in the soil in presence of potash and soda derived from the decomposition of the slates on which the soil rests. The potassium nitrate has reached the surface by capillary action, whilst the more soluble sodium nitrate has been washed down by the rains to the drier and hotter districts along the coast. Fossil bones are very common in the district, and it is possible that this deposit at Arané, which is sufficient to supply saltpetre to the whole world, is the product of the decomposition of a gigantic deposit of prehistoric animals. C. H. B.

**Pinnoite, a New Borate from Stassfurt.** By H. STAUTE (*Ber.*, 17, 1584—1586).—This mineral differs in its chemical and physical properties from the borates previously found at Stassfurt. It has a sulphur or straw-yellow colour, but is sometimes green, with a shade of red or grey. Hardness is 3—4; sp. gr. = 2·27. Its formula is  $\text{MgB}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ . When heated, it decrepitates, becomes white, and melts with some difficulty, imparting a green coloration to the flame. Mineral acids dissolve it readily on heating. When boiled with water, an alkaline liquid is obtained, from which a flocculent precipitate separates, but redissolves as the solution cools. A. K. M.

**Haydenite.** By H. N. MORSE and W. S. BAYLEY (*Amer. Chem. J.*, 6, 24—25).—This mineral from Baltimore was first described as an independent species by Cleaveland, and confirmed by Levy's assertion of its monosymmetric form. J. D. Dana and Des Cloizeau have, however, found the mineral to be really rhombohedral, like chabazite; but the only two published analyses by B. Silliman and Delesse do not agree with each other, or with Rammelsberg's formula for chabazite. The author has analysed an apparently undecomposed material, with the result that its composition agrees with the

chabazite formula, and haydenite is, therefore, chemically and physically identical with chabazite.

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	BaO.	K <sub>2</sub> O.	H <sub>2</sub> O.	
49·29	18·06	0·79	5·13	0·86	1·46	3·16	21·31	= 100·07
49·19	18·07	0·88	5·19	0·86	1·48	2·84	21·31	= 99·81
								H. B.

**Avalite.** By S. M. LOSANITSCH (*Ber.*, **17**, 1774—1775).—Avalite is the name the author gives to a new chromium mineral which he has obtained from the neighbourhood of Mount Avala, near Belgrade. This mineral occurs in clay, and many minerals from that district, in the form of small green scales. The author freed it from clay, &c., by levigation, the mineral being specifically lighter than the clay. This mineral is not attacked by the ordinary acids, but is easily decomposed by means of hydrofluoric acid, or by fusion with alkaline carbonates. The analyses gave the following results:—

	I.	II.	III.
SiO <sub>2</sub> .....	56·13	55·59	61·52
Cr <sub>2</sub> O <sub>3</sub> .....	14·59	10·39	9·82
Al <sub>2</sub> O <sub>3</sub> .....	14·37	16·60	14·14
K <sub>2</sub> O .....	3·54	3·69	2·51
Fe <sub>2</sub> O <sub>3</sub> .....	1·10	2·55	1·28
MgO .....	0·43	1·74	1·20
Chromite .....	1·68	1·80	3·43
H <sub>2</sub> O (hygroscopic).	2·39	1·39	0·73
Loss on ignition ..	5·38	5·42	4·48
	99·61	99·17	99·11

The author considers the water, chromite, iron, and magnesium to be impurities. The green colour of much of the quarzite occurring in serpentine from the district of Belgrade is due to the presence of avalite.

L. T. T.

**Origin of Phosphorites and Ferruginous Clays in Limestone Districts.** By DIEULAFAIT (*Compt. rend.*, **99**, 259—262).—From numerous analyses of phosphorites and the associated rocks, the author concludes that the calcium phosphate existing in the caverns in the south-west of France does not represent one-tenth of that which existed in the limestone which has been removed during the formation of the caverns. The ferruginous clays which accompany and often cover the phosphates have the same composition as the residue obtained when the rocks forming the walls of the cavern are treated with a dilute oxidising acid. Substances such as manganese, nickel, cobalt, zinc, copper, and iodine, which exist in very small quantities in the ordinary rocks of the phosphatic districts, are found in relatively high proportion in the phosphorite and the clays associated with it. It is possible, therefore, that the phosphorites in the south-west of France have been extracted from the surrounding rocks by chemical reactions in the wet way.

C. H. B.

**The Granite District of the Black Forest.** By J. H. KLOOS (*Jahrb. f. Min.*, 1884, 1, 66).—The principal rock of the middle portion of the Wiesen Valley is a coarsely granular biotite-granite, which differs from the ordinary granite of the Black Forest in that muscovite is always absent. In this granitic mass, other crystalline rocks are frequently met with, both in veins and in irregular masses. The description of these rocks in the neighbourhood of the Wiesen Valley, forms the subject of this paper, special attention being paid to the diorites and gabbro of Ehrberg, Waldmatt, and Kastel.

This granitic district of the southern portion of the Black Forest presents remarkable examples of the structural and physical differences between minerals of the same or similar composition from the older and more recent massive rocks, and also of the alterations and decompositions to which these minerals have been subjected after they have built up the rocks. The structure and physical properties of the orthoclase, the principal mineral in the predominating biotite-granite, are totally different from those of the potash felspar usually met with in similar districts of the more recent crystalline rocks. A labradorite, perfectly and uniformly filled with a powder rich in manganese, like that presented in the Ehrberg gabbro, is unknown in more recent eruptive rocks. Diabase and the green radiated hornblende occur in this district in a form totally different from that usual in trachytes, basalts, and other more recent rocks. The occurrence of the quartz proves that it has crystallised out under unusual conditions, or that subsequent metamorphism has, to a great extent, taken place. An excellent example of the subsequent alteration of a mineral by the action of water is presented by the conversion of labradorite into an albite and zeolitic mineral. The various stages of this alteration may be seen both in the granite itself and in the rock masses subordinate to it. As examples may be mentioned the alteration of the plagioclase from the granitic and dioritic rocks into mica-like minerals, finally resulting in perfect pseudomorphs; and secondly, the alteration of the biotite of the finely granular granites into mica, which occurs to a small extent in the Ehrberg diorite, and in a very well-marked manner in the Kastel gabbro; the alteration of the biotite of the finely granular granites into a soft scaly inelastic substance; the alteration of olivine into serpentine in the Ehrberg picrite; the alteration of augite or hornblende in the minettes into a new fibrous yellow mineral, the exact nature of which has not yet been determined; and the alteration of the pinite and other constituents in the pinite-porphry, are further examples.

B. H. B.

**Mica-diorites and Kersantites of Southern Thuringia and the Frankenwald.** By R. PÖHLMANN (*Jahrb. f. Min.*, 1884, *Beilage*, 67—160).—The vein rocks, rich in mica, occurring in the northern flank of the Fichtelgebirge, described by Gümbel as “lamprophyry,” are, for the most part, kersantites; mica-diorites and minettes occur to a smaller extent. The kersantites are porphyritic rocks, and contain as constituents brown magnesium mica, felspar, augite partially replaced by hornblende, quartz, calcite, titanite, apatite, magnetite, and chromite. The magnesium mica was always found to be optically

biaxial. It probably belongs partly to anomite, and partly to mer-oxene. In order to determine the chemical nature of the magnesium mica, that from the Bärenstein rock was analysed, giving the following results:—

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Mn <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.
38·72	0·75	16·26	trace	7·40	5·25	1·86	18·74
K <sub>2</sub> O.	Na <sub>2</sub> O.	F.	H <sub>2</sub> O.	Total.	Sp. gr.		
8·89	trace	trace	2·60	100·47	2·88		

The felspar is, for the most part, triclinic (oligoclase, labradorite); but orthoclase is also present. The rather light coloured monoclinic augite on decomposing hardly ever passes into uralite, but into chloritic products. The presence of chromite crystals is worthy of note. The calcite is always of a secondary nature. The same is, to a certain extent, true of the quartz, if the porphyritic crystals are not taken into account.

The mica diorites are sometimes rich in augite and hornblende, as, for example, in the rock from Marlesreuth; at other times these bisilicates are entirely wanting, as is the case in the rock from Ködelschutz.

Contact alterations of the kersantite were observed, both in the rock itself and in the limestones and slates, but they are of slight importance. The kersantites do not essentially differ in structure and mineralogical composition from those known in other districts. The term "lamprophyre" is consequently incorrect from a petrographical point of view, more especially as it was used as a collective name for rocks of different classes.

B. H. B.

**Composition of the Water of the New Mineral Springs at Freyersbach.** By K. BIRNBAUM (*Ber.*, 17, 1614—1615).—The com-

*Parts per 10,000.*

	Alfred's spring.	Friedrich's spring.	Lithion's spring.
Ferrous bicarbonate .....	0·4410	0·5875	0·3040
Calcium bicarbonate .....	10·3995	15·2750	15·2425
Magnesium bicarbonate .....	3·0778	4·4949	4·6233
Tricalcium phosphate.....	0·0500	0·0075	traces
Calcium sulphate.....	0·0843	0·1465	0·1197
Potassium sulphate.....	0·3369	2·3962	2·7954
Sodium sulphate .....	6·2008	6·9940	6·5662
Sodium bicarbonate.....	1·0206	2·3499	2·1930
Magnesium chloride .....	0·2426	0·1967	0·2869
Lithium chloride.....	0·0917	0·1300	0·1754
Silicic acid .....	0·9308	1·0841	1·0236
Carbonic anhydride.....	16·7847	19·7149	16·6063
Nitrogen .....	0·0130	1·5525	0·0161
Total .....	40·1737	54·9297	49·9524

position of this water is similar to that of the mineral water examined by Bunsen (*Zeit. Anal. Chem.*, 1871, **10**, 391), but differs from the latter in the proportion of the constituents, and in containing a considerable amount of lithium salts, as shown in the table, p. 1274.

*Gaseous Constituents. Number of Cubic Centimeters in 10,000 grams Water.*

	Alfred's spring.	Friedrich's spring.	Lithion's spring.
Total carbonic anhydride .....	13,434·9	17,219·5	15,546·2
Loosely combined do. ....	2,447·2	3,594·0	3,548·3
Total combined do. ....	4,894·4	7,188·0	7,096·6
Free carbonic anhydride.....	8,540·5	10,031·5	8,449·6
Nitrogen .....	10·3	1,235·9	12·8
Temp. of water (that of the air being 10·4°)	11·7°	11·6°	11·5°
Sp. gr. at 12° .....	1·0025	1·0035	1·0025

A. K. M.

## Organic Chemistry.

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### Properties of Liquid Methane and its Use as a Refrigerator.

By S. WROBLEWSKI (*Compt. rend.*, **99**, 136—137). — The methane employed was obtained by heating sodium acetate with soda-lime, and was liquefied by means of liquid ethylene. Its critical temperature is  $-73.5^{\circ}$  and the critical pressure 56.8 atmos. The following table shows the relation between the boiling point and the pressure :—

Atmos.	Boiling point.
56.8	— $73.5^{\circ}$
52.5	— $75.9$
24.9	— $98.2$
16.4	— $113.4$
6.7	— $130.9$

At atmospheric pressure, methane does not solidify, but boils between  $-155$  and  $-160^{\circ}$ , and thus gives a temperature intermediate between those obtained with liquid oxygen and liquid ethylene respectively.

C. H. B.

**Behaviour of Ethylidene Chloride with Ethylamine and Amylamine.** By A. W. HOFMANN (*Ber.*, **17**, 1907—1908).—When ethylidene chloride is heated with ethylamine, collidine and ethyl chloride are formed, together with small quantities of ammonia and triethylamine :—

- I.  $4\text{C}_2\text{H}_4\text{Cl}_2 + 7\text{NH}_2\text{Et} = \text{C}_8\text{H}_{11}\text{N}, \text{HCl} + 6\text{NH}_2\text{Et}, \text{HCl} + \text{EtCl}$ .  
 II.  $3(\text{NH}_2\text{Et}, \text{HCl}) = 2\text{NH}_4\text{Cl} + \text{NEt}_3\text{HCl}$ .

Amylamine yields collidine, diamylamine, triamylamine, and ammonium chloride.

Acetamide also yields collidine, together with acetic chloride.

L. T. T.

**Action of Chlorine on Isobutylene.** By CHÉCHOUKOFF (*Bull. Soc. Chim.*, **41**, 253—254).—The action of chlorine on isobutylene does not give rise to a chloride of that hydrocarbon, but to two isomeric chlorisobutylenes. The first, *isocrotyl chloride*,  $\text{CMe}_2\text{:CHCl}$ , forms isobutaldehyde when the aqueous solution is heated; and when warmed with sodium ethylate, it yields *ethyl isocrotyl ether*. The second *chlorisobutylene* distils at  $72\text{--}78^\circ$ , and is insoluble in water. On heating it with a solution of potassium carbonate, it yields an alcohol boiling at  $111\text{--}115^\circ$ . This combines with bromine, forms a crystalline alcoholate, and evolves hydrogen chloride when treated with phosphorus pentachloride. The corresponding ethereal acetate boils at  $119\text{--}121^\circ$ . The constitution of this chlorisobutylene is probably  $\text{CH}_2\text{:CMe.CH}_2\text{Cl}$ , and that of the alcohol  $\text{CH}_2\text{:CMe.CH}_2\text{OH}$ .

W. R. D.

**Caucasian Petroleum.** By MARKOWNIKOFF and OGLOBINE (*Bull. Soc. Chim.*, **41**, 258).—Hydrocarbons of the  $\text{C}_n\text{H}_{2n}$  series, called by the authors *naphthenes*, constitute the principal part of Caucasian petroleum. The members of this group of hydrocarbons do not form nitro-derivatives, and resemble the paraffins in not yielding additive compounds, and also in the formation of alcohols from the chlorinated derivatives. Certain of the chlorinated derivatives are convertible, by abstraction of hydrogen chloride, into hydrocarbons of the  $\text{C}_n\text{H}_{2n-2}$  series, which behave like unsaturated compounds, and may be termed *naphthylenes*.\* When oxidised, the naphthenes form oxidation-products or are converted into higher isologues, and thus possess all the characters of closed-chain hydrocarbons. The portion of Caucasian petroleum having a higher boiling point, probably contains hydrocarbons of the  $\text{C}_n\text{H}_{2n-2}$  and  $\text{C}_n\text{H}_{2n-4}$  series, whilst 10 per cent. of the petroleum consists of benzenoid hydrocarbons belonging to known series, and also to a series of hydrocarbons isomeric with styrolene and its isologues. These compounds furnish brominated derivatives, but no additive compounds. Their benzenoid character is exhibited in the formation of nitro- and sulpho-derivatives. The petroleum also contains acid and neutral compounds containing oxygen.

W. R. D.

**Preparation of Cyanides and Ferrocyanides from Trimethylamine.** By E. WILLM (*Bull. Soc. Chim.*, **41**, 449—451).—This paper describes the commercial application of the decomposition of trimethylamine at a red heat by which the whole of the nitrogen is obtained as hydrocyanic acid and ammonium cyanide, together with

\* It would be better, perhaps, to call these hydrocarbons naphthines (analogous to ethine), seeing that the term naphthyl has long been used to signify the hypothetical radical  $\text{C}_{10}\text{H}_7\text{—C}$ . E. G.



gaseous hydrocarbons. The vapour of trimethylamine is passed into a retort heated to bright redness, and the products are passed first into sulphuric acid, where the ammonium cyanide is converted into hydrocyanic acid; and secondly into a solution of soda, potash, or calcium hydroxide, where the acid is converted into the corresponding cyanide. In this way, concentrated solutions of the cyanides are obtained, while the gaseous hydrocarbons, free from ammonia and hydrogen cyanide, pass on and are collected for use in lighting the works. From the solution of alkaline cyanide, the corresponding ferrocyanide is obtained by adding ferrous oxide, freshly precipitated from a solution of ferrous chloride by milk of lime, and this liquid after filtering yields, without further concentration, crystals of ferrocyanide, which are as pure as those obtained after the third crystallisation by the older method. The process appears to have an important bearing on the economical utilisation of the residues from molasses.

W. R. D.

**Constitution of some Simple Cyanogen-compounds.** By G. CALMELS (*Compt. rend.*, 99, 239—241).—When finely powdered mercuric cyanide is heated with an equal weight of methyl iodide in sealed tubes at  $110^{\circ}$ , the products are mercuric iodide, methylcarbamine, and a tarry substance formed by the polymerisation of the carbamine at the moment of its formation. Zinc cyanide must be boiled for at least two days with ethyl iodide (in a flask with an inverted condenser), in order to obtain an appreciable quantity of ethylcarbamine. The failure of this reaction with certain cyanides is due to the fact that the conversion of these cyanides into iodides requires a temperature at which the carbamine is decomposed.

When an ethereal solution of zinc-ethyl is mixed with an ethereal solution of cyanogen iodide, zinc cyanide is precipitated and ethyl iodide is formed. The addition of an ethereal solution of cyanogen iodide to dry zinc methyl iodide, however, produces a considerable development of heat, and zinc iodide, zinc cyanide, methyl iodide, and methylcarbamine are formed. When an ethereal solution of mercuric methide is heated with an equivalent quantity of cyanogen iodide in a sealed tube at  $50^{\circ}$ , mercuric cyanide is formed; but if the temperature is raised to  $100^{\circ}$ , the inverse reaction takes place and ethylcarbamine is produced. The action of cyanogen iodide in ethereal solution on metallic zinc yields zinc cyanide and free iodine, the latter slowly combining with the excess of zinc. It is evident that in these reactions the metallic cyanide is formed in preference to the iodide, but this fact does not determine the constitution of cyanogen iodide, for a metallic cyanide is always an intermediate product of the action of this substance on organo-metallic radicles. When, however, an ethereal solution of aluminium-ethyl is mixed with a similar solution of cyanogen iodide, aluminium iodide and acetonitrile are produced, but no trace of ethylcarbamine is formed. It follows that the constitution of cyanogen iodide is represented by the formula  $\text{N}\equiv\text{C}-\text{I}$ , and is strictly analogous to the constitution of the chloride and bromide.

These reactions confirm the existence of two distinct groups,

cyanides and isocyanides, amongst the most simple compounds of cyanogen.

C. H. B.

**Ethereal Salts of Cyanuric Acid.** By PONOMAREFF (*Bull. Soc. Chim.*, **41**, 315).—The ethereal salts of cyanuric acid were obtained by the action of sodium methoxide and ethoxide on cyanogen iodide or bromide, or on the polymerides of the latter. These compounds combine with mercuric chloride, and when ethyl cyanurate is heated at 180–200°, it is converted into ethyl isocyanurate. Heated to a moderate extent with baryta-water, *barium diethyl isocyanurate* is formed; the corresponding acid is isomeric with that obtained by Limpricht. The ethereal salt can be reformed by heating the lead salt of the acid with ethyl iodide. The acid obtained by decomposing the ethereal salts of cyanuric acid with potash is identical with that derived from carbamide. The same ethereal salts can be obtained by heating the silver salt of cyanuric acid with ethyl or methyl iodide, but there are also produced the corresponding salts of isocyanuric acid. When monopotassium and dipotassium cyanurates are treated in a similar manner at 180°, the first salt gives rise to the diethyl-derivative, and the second salt to the triethyl-derivative of cyanic acid. The author concludes that the salts of the formula (CONEt)<sub>3</sub> are more stable than those of the formula (CNOEt)<sub>3</sub>.

W. R. D.

**Specific Volumes of Normal Fatty Acids and Alcohols.** By A. ZANDER (*Annalen*, **224**, 56–95).—The author has determined the sp. gr. and specific volume of the following compounds:—

	Boiling point.	Sp. gr. at 0°.	Sp. gr. at the boiling point.	Spec. vol.
<i>Acids.</i>				
Formic .....	100·8	1·2415	1·1175	41·1
Acetic .....	118·1	1·0701	0·9372	63·8
Propionic .....	141·8	1·0133	0·8589	86·0
Normal butyric .....	162·4	0·9746	0·8099	108·4
Iso „ .....	154·1	0·9651	0·8054	108·9
Normal valeric .....	185·4	0·9562	0·7828	130·0
„ caproic .....	204·7	0·9446	0·7589	152·5
„ heptolic .....	223·2	0·9313	0·7429	174·6
„ octoic .....	236·5	0·9270	0·7264	197·8
<i>Alcohols.</i>				
Methyl .....	66·2	0·8111	0·7483	42·6
Normal propyl .....	97·4	0·8177	0·7369	81·2
„ butyl .....	117·5	0·8233	0·7247	101·9
„ amyl .....	137·8	0·8282	0·7117	123·4
„ hexyl .....	157·3	0·8312	0·6958	146·2
„ heptyl .....	175·8	0·8342	0·6876	168·3
„ octyl .....	195·5	0·8375	0·6807	190·6

The author has also determined the rate of expansion of these liquids. The following table shows the volume they occupy at different temperatures, the volume at 0° being taken as unity:—

Alcohols.	10°.	20°.	30°.	50°.	80°.	130°.	150°.
Normal propyl.....	1·0082	1·0174	1·0273	1·0494	1·0865	—	—
Iso „ .....	1·0108	1·0218	1·0332	1·0577	1·1001	—	—
Normal butyl.....	1·0087	1·0179	1·0277	1·0489	1·0847	—	—
„ amyl.....	1·0091	1·0183	1·0276	1·0470	1·0796	1·1502	—
„ hexyl.....	1·0087	1·0177	1·0270	1·0469	1·0804	1·1488	1·1816
„ heptyl.....	1·0083	1·0167	1·0254	1·0435	1·0736	1·1362	1·1671
„ octyl.....	1·0080	1·0162	1·0247	1·0427	1·0729	1·1320	1·1594

Acids.	10°.	20°.	50°.	100°.	150°.	200°.
Formic .....	1·0097	1·0196	1·0509	1·1100	—	—
Acetic .....	1·0106	1·0213	1·0542	1·1159	—	—
Propionic .....	1·0106	1·0214	1·0559	1·1199	—	—
Normal butyric.....	1·0104	1·0210	1·0540	1·1149	1·1853	—
Isobutyric .....	1·0110	1·0205	1·0544	1·1184	1·1895	—
Normal valeric .....	1·0098	1·0198	1·0507	1·1068	1·1705	—
„ caproic.....	1·0095	1·0192	1·0493	1·1039	1·1660	1·2375
„ heptoic.....	1·0087	1·0176	1·0459	1·0984	1·1570	1·2216
„ octoic .....	1·0092	1·0185	1·0469	1·0974	1·1542	1·2204

W. C. W.

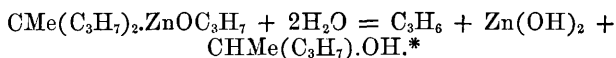
**Action of Aluminium Chloride on a Mixture of Alcohols of the Paraffin Series with Ethyl Chlorocarbonate.** By B. PAWLEWSKI (*Ber.*, 17, 1606—1607).—The author finds this reaction is similar to that recently described by him in which ethyl phenylcarbonate is produced (this vol., p. 1005). Aluminium chloride, in considerable excess, is added gradually to a mixture of propyl alcohol with ethyl chlorocarbonate, and the whole allowed to remain for several hours; the mass is then warmed, when a violent action sets in accompanied by an abundant evolution of hydrochloric acid. The product is treated with water and a 10 per cent. solution of hydrochloric acid, then dried and fractioned. The ethylic propylcarbonate,  $\text{PrO.COOEt}$ , obtained boils at  $145\cdot6^\circ$  (corr.); its sp. gr. is  $0\cdot9532$  at  $20^\circ$ .  
A. K. M.

**Purification of Methyl Alcohol.** By J. REGNAULD and VILLEJEAN (*Compt. rend.*, 99, 82—84).—Methyl alcohol prepared from methyl oxalate almost always contains small quantities of some substance, possibly either acetone or ethyl alcohol, which yields iodoform when treated with iodine. To obtain perfectly pure methyl alcohol, the alcohol prepared from the oxalate is mixed with 10 per cent. of iodine, and sodium hydroxide added gradually until the reaction is distinctly alkaline. The liquid is then carefully distilled. In this

process the foreign organic substances are converted into iodoform, and the latter is decomposed by the alkali into an iodide and a formate.

The peculiar saffron-like odour observed when iodine is mixed with an aqueous solution of potash or soda was obtained by the authors with iodine liberated by the action of chlorine on a solution of fused potassium iodide in water distilled with potassium permanganate, and recently fused sodium hydroxide. The glass vessels containing these substances had previously been strongly heated, and were exposed to the air as little as possible. It is evident therefore that if the odour is due to iodoform formed from traces of organic matter, the quantity of iodoform must be infinitesimal. C. H. B.

**Action of Zinc Propyl on Acetic Chloride.** By MARKOWNIKOFF (*Bull. Soc. Chim.*, **41**, 259—260). From analogy, it was expected that the reaction of zinc propyl with acetic chloride would give the tertiary alcohol, *methyl dipropyl carbinol*, but it is found to yield the secondary alcohol, *methyl propyl carbinol*, and propylene. This is explained by the action of water on the unstable compound  $\text{CMePr}_2\text{ZnOPr}$ , thus:—



W. R. D.

**Cetyl Alcohol and Cetylacetic Acid.** By F. KRAFFT (*Ber.*, **17**, 1627—1631). In a previous paper (Abstr., 1883, 1075) the author described the preparation of hexadecyl alcohol by the reduction of palmitaldehyde, and proved its identity with the chief constituent of "cetyl alcohol" from spermaceti. Commercial cetyl alcohol (m. p. 45—47·5°) contains also *octodecyl alcohol*,  $\text{C}_{18}\text{H}_{36}\text{O}$ , and probably some lower homologues. The hexadecyl alcohol and octodecyl alcohol may be separated by converting the mixture into the acetic ethers and fractioning. The purified octodecyl alcohol crystallises in white scales, melts at 5·9°, and boils at 210° (15 m.m.), agreeing with the alcohol obtained from stearaldehyde (*loc. cit.*). To obtain cetylacetic acid, cetylmalonic acid is first prepared by the action of sodium ethylate on ethyl malonate and cetyl iodide. Cetylmalonic acid,  $\text{C}_{19}\text{H}_{36}\text{O}_4$ , melts at 120—121°, and begins to decompose at about this temperature, whilst at 150—180° it rapidly breaks up into carbonic anhydride and *cetylacetic acid*,  $\text{C}_{18}\text{H}_{34}\text{O}_2$ . After purification this melts at 69·2°, crystallises in large nacreous plates, and is identical with ordinary (normal) stearic acid. Guthzeit states that the two are isomeric (Abstr., 1881, 408). A. K. M.

**Chemical Composition of Carnauba Wax.** By H. STÜRCKE (*Annalen*, **223**, 283—314).—Carnauba wax is obtained from *Copernicia cerifera*, a Brazilian palm. It has been investigated by Berard (*Bull. Soc. Chim.* [1], **9**, 41), Story-Maskelyne (this Journal, 1869, 87), and

\* This equation is obviously incorrect. Arguing from Butlerow's results, the reaction should probably be represented,  $\text{CMe}(\text{C}_3\text{H}_7)_2\text{ZnOC}_3\text{H}_7 + 2\text{H}_2\text{O} = \text{C}_3\text{H}_6 + \text{C}_3\text{H}_8 + \text{Zn}(\text{OH})_2 + \text{CHMe}(\text{C}_3\text{H}_7)\text{OH}$ .—W. R. D.

Piverling, who all find it to consist mainly of myristyl cerotate. In the alcoholic extract of the wax, Berard found free cerotic acid; Story-Maskelyne, on the contrary, found free myricyl alcohol, whilst Piverling found the substance soluble in boiling alcohol to be distinguished from myricyl alcohol by its melting point and elementary composition.

Carnauba wax forms a hard, brittle, amorphous, straw-yellow mass, melting at  $83-83.5^{\circ}$ . In confirmation of Story-Maskelyne's statement, myricyl alcohol dissolves out on boiling with alcohol; it is accompanied by a small quantity of myricyl cerotate, which is soluble in boiling alcohol to the extent of about 0.82 gram per litre. The wax was saponified by boiling it with alcoholic soda. The non-acid constituents were separated by fractional solution in and crystallisation from light petroleum and subsequently from alcohol. There were thus obtained: 1. A crystalline hydrocarbon of paraffin-like nature, melting at  $59-59.5^{\circ}$ , and resolidifying at  $58.7^{\circ}$ ; 2. A crystalline alcohol of the formula  $C_{27}H_{56}O$ , melting at  $76^{\circ}$ ; on heating this with soda-lime, &c., it is converted into an acid melting at  $78.1-78.4^{\circ}$ ; 3. Myricyl alcohol,  $C_{30}H_{62}O$ , free and in combination (as myricyl cerotate), forming about 45 per cent. of the wax employed. It crystallises in lustrous white tables, melts at  $85.5-85.7^{\circ}$ , resolidifies at  $85.3^{\circ}$ , is sparingly soluble in the cold, but readily in hot alcohol, ether, benzene, light petroleum, and chloroform. By heating it with soda-lime, it is converted into *melissic acid*; the formula  $C_{30}H_{60}O_2$  for this acid is confirmed by fresh analyses of the acid, and of its lead and silver salts. It crystallises in lustrous white plates or needles, melts at  $89.9-90.2^{\circ}$ , resolidifies at  $89.2^{\circ}$ , is readily soluble in hot alcohol, light petroleum, chloroform, and carbon bisulphide, sparingly in boiling ether. The *lead salt* melts at  $118-119^{\circ}$ , and resolidifies at  $117.5^{\circ}$ , it is sparingly soluble in boiling toluene and glacial acetic acid, insoluble in alcohol and ether; 4. A *dihydric alcohol* of the formula  $C_{23}H_{46}(CH_2.OH)_2$ . It forms a pure white microcrystalline powder or fine needles, melts at  $103.5-103.8^{\circ}$ , resolidifies at  $102.5^{\circ}$ , is sparingly soluble in light petroleum, more readily in a mixture of benzene and ether. By heating it with soda-lime, &c., it is converted into a *bibasic acid*, which forms white crystalline flocks, melts at  $102.5^{\circ}$ , and resolidifies at  $100.2^{\circ}$ ; it is soluble in boiling alcohol, benzene, and a mixture of ether and light petroleum. The *lead salt*,  $C_{23}H_{46}(COO)_2Pb$ , is insoluble in boiling ether, alcohol, and benzene, scarcely soluble in boiling toluene, readily in boiling glacial acetic acid. It is decomposed when heated to  $125^{\circ}$ .

The separation of the acids obtained by the saponification proved exceedingly troublesome, and was effected by a combined process of fractional solution in light petroleum, and fractional precipitation with magnesium acetate. The products obtained were: 1. An acid of the formula  $C_{23}H_{47}.COOH$ , isomeric with lignoceric acid, and occurring only in small quantity. It forms a fine crystalline powder, melts at  $72.5^{\circ}$ , resolidifies at  $71.8^{\circ}$ , is readily soluble in boiling alcohol, ether, light petroleum, and benzene. The *lead salt*,  $(C_{23}H_{49}O_2)_2Pb$ , melts at  $110-111^{\circ}$ , and resolidifies at  $108-109^{\circ}$ ; 2. The main acid constituent is either identical or isomeric with cerotic acid,  $C_{27}H_{54}O$ .

It agrees with cerotic acid from bees-wax in all its properties, except that after fusion the resolidified acid exhibits no trace of crystalline structure; 3. A substance of lactone-like nature presumably of the formula  $C_{19}H_{38} < \begin{smallmatrix} CH_2 \\ CO \end{smallmatrix} > O$ . It forms a white crystalline powder, melts at  $103.5^\circ$ , is sparingly soluble in boiling 90 per cent. alcohol, somewhat more soluble in absolute alcohol, benzene, and toluene, readily in boiling isobutyl alcohol. When heated with soda-lime, &c., it yields a bibasic acid, melting at  $89.5-90^\circ$ , whose lead salt on analysis gave numbers agreeing with the formula  $C_{19}H_{38}(COO)_2Pb$ .

A. J. G.

**Action of Sulphur on Sodium Mercaptide.** By H. BÖTTGER (*Annalen*, **223**, 346—348).—Sulphur when heated at  $100^\circ$  with sodium mercaptide in presence of absolute alcohol yields ethyl bisulphide and sodium polysulphides. Experiments were made to find a readier method of preparing sodium mercaptide; by the action of ethyl sulphide on sodium sulphide; of mercaptan on sodium hydrosulphide; of ethyl sulphide on sodium hydrosulphide; and of sodium sulphide on mercaptan, but in each case with negative results.

A. J. G.

**Ethyl Sulphides.** By H. BÖTTGER (*Annalen*, **223**, 348—354). According to Müller (this Journal, 1871, 904), sulphur does not act on ethyl sulphide even on heating the mixture for four days at  $150^\circ$ . The author finds that by heating the mixture for 24 hours at  $180^\circ$ , the monosulphide is in part converted into di-, tri-, tetra-, and probably also penta-sulphide.

Sulphur chloride acts violently on ethyl sulphide, hydrochloric acid being evolved, carbon separating, and ethyl polysulphides being formed.

Sulphurous dichloride when mixed with ethyl sulphide, and gently heated, reacts with it to form hydrochloric acid, sulphurous anhydride, carbon, and ethyl polysulphides. Sulphuric dichloride reacts in a similar manner.

By the action of sulphuric hydroxychloride on ethyl sulphide, there are formed sulphuric acid, sulphurous anhydride, hydrochloric acid, and water, whilst carbon separates.

A. J. G.

**A New Ethylic Phosphate.** By A. GEUTHER (*Annalen*, **224**, 274—282).—An ethylic phosphate of the composition  $(EtO)_3H.P.O.P(OEt)_4$ , is obtained when phosphorous trichloride acts on an excess of sodium ethylate (which has been dried at  $180^\circ$  in an atmosphere of hydrogen) in the presence of absolute ether. Alcohol, ethylene, and ethyl phosphine, are also formed during the reaction. The new phosphate is a colourless liquid lighter than water. It boils between  $150^\circ$  and  $160^\circ$ , with gradual decomposition into alcohol and ethyl phosphite and phosphate.

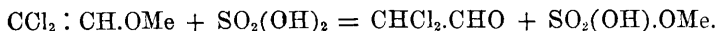
W. C. W.

**Dichlorovinyl Methyl Ether.** By A. DENARO (*Gazzetta*, **14**, 117—120).—The four known vinyl ethers are, vinyl ethyl ether,  $C_2H_3.OEt$ ; monochlorovinyl ethyl ether,  $C_2H_2Cl.OEt$ ; dichlorovinyl ethyl ether,  $C_2HCl_2.OEt$ ; and trichlorovinyl ethyl ether,  $CCl_3.OEt$ ,

but up to the present time vinyl methyl ether and its derivatives have not been examined.

*Dichlorovinyl methyl ether*,  $C_2HCl_2.OMe$ , is prepared by heating potassium methyrate (144 grams) with trichlorethylene (104 grams) for 16 hours at  $50-60^\circ$ , in a flask furnished with a reflux condenser; water is then added, and the ether which separates is dried over calcium chloride, and fractionally distilled to separate the small portion of unattacked trichlorethylene. The ether is a colourless liquid of agreeable odour, recalling that of acetal. It boils at  $109-110^\circ$ , and its sp. gr. is 1.2934 at  $0^\circ$  and 1.1574 at  $100^\circ$ . When exposed to the air, it slowly decomposes with evolution of hydrochloric acid.

When the ether is boiled with sulphuric acid diluted with four parts of water in a reflux apparatus, it is decomposed with formation of a crystalline substance, which may be extracted from the product by skaking it with ether: this melts at  $56-57^\circ$ , distils at  $118-121^\circ$ , and appears to be identical with Paternò's dichloraldehyde; the reaction in which it is formed being



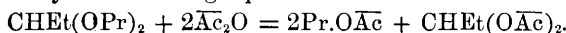
From its mode of formation and the action of sulphuric acid on it, there can be no doubt that the constitutional formula of the ether is  $CCl_2 : CH.OMe$ .  
C. E. G.

**Allyl Dimethyl Carbinol.** By POUTOKINE (*Bull. Soc. Chim.*, **41**, 268).—The fractional distillation of crude allyl dimethyl carbinol yields an alcohol boiling at  $174^\circ$ , which is attacked by bromine, hydrobromic acid being evolved, and when oxidised it yields acetic and butyric acids. It probably, therefore, contains the isopropyl-group, and may be represented as  $C_3H_7.CH : CH.CH_2.CMe_2.OH$ .

W. R. D.

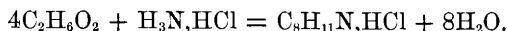
**Dipropyl Propylidenic Oxide.** By B. SCHUDEL (*Monatsh. Chem.*, **5**, 245—250).—This compound is formed by the action of phosphine on a mixture of normal propyl alcohol and propaldehyde, but only in small quantities. A much better yield is obtained by heating a mixture of the alcohol and aldehyde with acetic acid in sealed tubes at  $100^\circ$ . The product is fractionated until the thermometer rises to  $110^\circ$ , and the residue is then heated with potash in a silver flask connected with a reflux condenser, for some hours; it is finally washed with water and dried over calcium chloride. In this manner a liquid is obtained, the chief portion of which boils at  $163-164^\circ$ , and consists of dipropyl propylidenic oxide,  $CHEt(OPr)_2$ . It is a liquid of sp. gr. = 0.8495 at  $0^\circ$ , and boils at  $165.6^\circ$  (corr.), and barometer at 747 mm. The determinations of its vapour-density gave the numbers 81.78 and 80.14 ( $H = 1$ ).

That the oxide is in reality dipropyl propylidenic oxide is shown by the fact that, when heated with acetic anhydride in sealed tubes at  $180^\circ$ , it yields propyl acetate and the compound  $CHEt(O\overline{Ac})_2$ , as represented by the following equation:—



P. P. B.

**Action of Ammonium Chloride on Glycol at High Temperatures.** By A. W. HOFMANN (*Ber.*, **17**, 1905—1906).—No trace of ethylenediamine is formed, but a pyridine base which proved to be collidine. The reaction must take place according to the equation



The temperature employed was 300—400°.

L. T. T.

**Butylic Glycerol Triacetin.** By L. PRUNIER (*Compt. rend.*, **99**, 193—195).—The butylic glycerol previously described (*Compt. rend.*, **80**, 1603), when heated with acetic anhydride in sealed tubes at 140°, yields a triacetin which can be obtained almost solid by evaporation over sulphuric acid and lime. It is a neutral substance with a bitter taste.

C. H. B.

**A General Reaction of Polyhydric Alcohols in Presence of Borax and Paratungstates.** By D. KLEIN (*Compt. rend.*, **99**, 144—147).—In presence of an aqueous solution of borax, dulcitol behaves in the same manner as mannitol (*Compt. rend.*, **86**, 826). Dulcitol is neutral to litmus, and borax is distinctly alkaline, but a solution containing less than 0.5 mol. of borax for each molecule of dulcitol is strongly acid, the acidity being greater the smaller the proportion of borax; a solution containing 0.5 mol. of borax for each mol. of dulcitol is neutral; and a solution containing a higher proportion of borax is alkaline, the alkalinity increasing with the amount of borax present. These results were obtained by mixing saturated solutions of the two substances at about 15°. None of the solutions showed any rotatory power. The acid solution first mentioned acquires an alkaline reaction when diluted with a large quantity of water.

With solutions of sodium paratungstate, dulcitol also behaves in the same way as mannitol. A mixture of concentrated solutions of the two substances has an acid reaction after boiling. The dulcitol solution, however, has no rotatory power. The solubility of dulcitol is largely increased by the presence of sodium paratungstate, and to a still greater extent by the presence of borax.

These reactions are perfectly general, and are produced by all biborates, soluble paratungstates, and all non-condensed polyhydric alcohols, the proportion of the alcohol required to produce an acid reaction being lower the higher the hydricity of the alcohol. Hydroxy acids, such as mucic acid, which contain a large number of OH groups, give similar reactions. An increase of rotatory power only takes place when the alcohol itself is optically active. Saccharose and dextrin do not give these reactions.

The reactions admit of very simple explanation. Ethereal salts of the alcohol employed are formed, and play the part of acids having a greater saturating capacity than the inorganic acid. They require for the formation of neutral salts a higher proportion of the base than was combined with the inorganic acid, and consequently give acid solutions.

C. H. B.



**Persite, a Sugar analogous to Mannitol.** By A. MUNTZ and V. MARCANO (*Compt. rend.*, 99, 38—40).—*Laurus persea*, a tree of moderate height, very abundant in the tropics, bears a fruit with a fleshy pericarp, rich in oil, and a ligneous-looking seed. In 1831 Avequin stated that this seed contained a large quantity of mannitol, and Melsens found that this mannitol has the same percentage composition as that derived from manna.

The sugar is easily extracted from the seeds by triturating them with boiling alcohol, or water containing a little basic lead acetate. It crystallises rapidly, and can be purified by repeated crystallisation from alcohol. It has the composition  $C_6H_{14}O_6$ , and melts at  $183.5$ — $184^\circ$ , like dulcitol, whereas the melting point of mannitol is  $164$ — $164.5^\circ$ . Unlike dulcitol, however, it yields oxalic acid without any mucic acid when oxidised with boiling nitric acid. This sugar, to which the author gives the name *persite*, is, in fact, analogous to but not identical with mannitol.

Persite is comparatively insoluble in cold water, a saturated solution at  $15^\circ$  containing only 6 per cent., but it is very soluble in hot water, from which it separates in a farinaceous mass on cooling. It is only very slightly soluble in cold alcohol, but its solubility increases with the temperature: a boiling saturated alcoholic solution, as it cools, deposits persite in a bulky mass of very slender needles. Persite even in concentrated solutions has no action on polarised light, but it acquires a distinct dextrorotatory power on adding borax to the solution. It has no action on an alkaline copper solution even after boiling with dilute inorganic acids, and it does not undergo true alcoholic fermentation.

When treated with a mixture of fuming nitric acid and sulphuric acid, persite yields a trinitro-derivative which detonates violently on percussion. Nitropersite is only slightly soluble in cold alcohol, but is somewhat soluble in boiling alcohol, from which it is deposited in a bulky crystalline mass. It is also somewhat soluble in ether. A solution in a mixture of alcohol and ether has a dextrorotatory power of  $+2.1$ .

When heated at about  $250^\circ$ , persite gives off water without becoming dark-coloured, and yields a substance analogous to mannan.

Persite occurs in the seeds of *Laurus persea* to the extent of 6 to 8 per cent.; in the pericarp from 1.8 to 6.3 per cent. according to the stage of maturity; and in the dry leaves about 2 per cent. When the fruit is completely ripe, the proportion of persite has considerably diminished, whilst that of oil has increased, and hence it would seem that persite, like mannitol in the olive, contributes to the formation of the fatty bodies. During the germination of the seeds the persite disappears.

C. H. B.

**Circular Polarisation of Cane-sugar.** By B. TOLLENS (*Ber.*, 17, 1751—1758).—About eight years ago, the author and Schmitz, working independently, both came to the conclusion, now generally accepted, that cane-sugar, as well as dextrose and some other substances investigated by Landolt, have no unchangeable specific

rotation, but that this decreases slowly as the concentration increases. Hesse's investigation of the rotation of very dilute solutions (*Annalen*, **176**, 89 and 189) seemed to show, however, that in solutions containing only 1 to 3 per cent. sugar, the rotation ( $[\alpha]_D = 68^\circ$  about) was much higher than those containing 10 per cent. and upwards ( $[\alpha]_D = 66.5-64^\circ$ ). The author has now made a careful series of determinations with very dilute solutions; he used a Landolt-Laurent instrument, and believes the results to be correct to within  $2'$ . He has found no such increase of rotation for dilute solutions, but if anything a *very slight* decrease; and concludes, therefore, that "the specific rotation of very dilute solutions of cane-sugar follows the same law as that of concentrated solutions," and that "only one equation is needed for calculating the specific rotation of cane-sugar solutions whatever their concentrations." The formula he previously gave (*Ber.*, **10**, 1410) for the specific rotation of concentrated solutions,  $[\alpha]_D = 66.386^\circ + 0.015035^\circ P - 0.0003986^\circ P^2$ , where  $P$  = percentage concentration of the solution, is applicable to all concentrations. The following table shows the results obtained compared with those calculated by means of the above formula.

Weight of sugar in 100 grams solution or P.	Rotation for $[\alpha]_D$ .		Difference.
	Found.	Calculated.	
grams.			
1.1062	66.341°	66.402°	- 0.061°
1.6767	66.499	66.410	+ 0.089
1.9870	66.276	66.414	- 0.148
2.0435	66.429	66.415	+ 0.014
3.0421	66.198	66.428	- 0.229
4.9850	66.450	66.451	- 0.001
6.8427	66.482	66.470	+ 0.012
9.0014	66.458	66.489	- 0.031
9.8963	66.454	66.496	- 0.042
34.8717	66.397	66.426	- 0.029
67.4507	65.529	65.587	- 0.058

The sugar employed was carefully purified by repeated crystallisation from water, and finally by precipitation from its aqueous solution by alcohol.

The author is at present carrying out similar investigations with dextrose, and already finds that the specific rotation decreases with dilution of the solution rather than increases.

L. T. T.

**Melitose from Cotton-seed.** By H. RITTHAUSEN (*J. pr. Chem.* [2], **29**, 351-357).—This sugar, which was discovered by Johnston in 1843, and further examined by Berthelot, has hitherto been found only in Tasmanian manna. The author finds that it is contained in large quantity in cotton-seed, and has prepared it from cotton-cake.

The cake is extracted with hot alcohol (sp. gr. 0.848), and the extract is concentrated, when it deposits crystalline lumps; these are washed with cold alcohol (80 per cent.) and then dissolved in alcohol heated to 70°; the solution is treated with animal charcoal and allowed to remain 3 to 5 days, when it deposits tufts of lustrous acicular crystals. The yield of pure melitose is 3 per cent. of the raw material. Melitose dissolves in 6 parts of water at 16°, and is almost insoluble in absolute alcohol. The aqueous solution has a higher dextro-rotatory power than cane-sugar:  $[\alpha]_D^{20} = 117.4^\circ$  (Berthelot gives  $[\alpha]_D^{20} = 88^\circ$  for the hydrates, and  $[\alpha]_D^{20} = 102^\circ$  for anhydrous melitose). It does not reduce Fehling's solution even on boiling. After boiling with dilute sulphuric acid, the rotatory power is reduced to about one-half the original,  $[\alpha]_D^{20} = 61.8^\circ$ , whilst Berthelot states that it is only reduced by one-third. The analysis agrees with the formula  $C_{12}H_{22}O_{11} \cdot 3H_2O$ . It undergoes partial fusion below 90°, and only loses the last traces of water very slowly, but if heated without fusion, the greater part of the water passes off at 84–85°, and the remainder is then readily removed at 104–108° without fusion.

P. F. F.

**Non-identity of Arabinose and Lactose.** By C. SCHEIBLER (*Ber.*, 17, 1729–1732).—Claesson (*Abstr.*, 1881, 795) has disproved Kiliani's view of the identity of arabinose and lactose (*Abstr.*, 1881, 243). C. O'Sullivan (*Trans.*, 1884, 41 *et seq.*) has described four different arabinoses obtained from gum arabic, and which he designates  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  arabinose. The author is inclined to think that O'Sullivan's  $\alpha$ -compound is identical with his arabinose, the  $\gamma$ -compound with lactose (galactose), and the  $\beta$ -compound a mixture of the two.

The author has prepared the phenylhydrazine compounds of arabinose and lactose. *Phenylarabinosazone* is precipitated in the form of oily drops which soon solidify, it melts at 157–158°. *Phenylgalactosazone* is precipitated at once in crystalline form and melts at 170–171°. E. Fischer found the melting point of the latter to be 182°.

L. T. T.

**New Method for Preparing and Estimating Glycogen.** By A. LANDWEHR (*Zeit. Physiol. Chem.*, 8, 165–174).—The extract of the liver, made in the ordinary way, is boiled with a small quantity of zinc acetate, to coagulate all the albumin. The filtrate from this precipitate is placed on the water-bath with an excess of ferric chloride, and, after heating, the whole of the iron is precipitated with soda. This precipitate is collected, washed with hot water, and dissolved in hydrochloric or acetic acid; the latter is preferable (in this case hydrochloric acid must also be added after solution): it is then poured into three times its volume of alcohol. The glycogen thus prepared is free both from ash and from nitrogen.

The quantitative determination can be made either by weighing the pure precipitated glycogen, after drying in a vacuum over sulphuric acid and in the water-oven at 120°, or by calculating as glycogen the difference between the iron precipitate weighed after

drying at 120° and the oxide of iron left after ignition. This, however, is open to objection, as the percentage of water is very variable in the excess of oxide of iron that must necessarily always be present.

J. P. L.

### Polarimetric Investigation of Various Forms of Cellulose.

By A. LEVALLOIS (*Compt. rend.*, 99, 43—45).—Cellulose prepared by the action of ferrous chloride solution on guncotton and on collodion pyroxylin was dissolved in an ammonio-copper solution, and the rotatory power of this solution compared with that of a similar solution of pure cellulose from paper, with the following results:—

	Deviation.
Pure cellulose .....	9.5°
Cellulose from trinitro-cellulose .	8.5
Cellulose „ pyroxylin .....	8.5

The differences observed may be attributed to hydration produced by prolonged washing of the reduced cellulose with hydrochloric acid. The product, in fact, had the appearance of hydrocellulose.

Similar determinations were made with a cuprammonium solution of cellulose which had been immersed in sulphuric acid of a definite strength for different periods of time. In the first series, the acid employed was sulphuric acid of 66°, diluted with its own volume of water, and in the second series the same acid diluted with only half its volume of water.

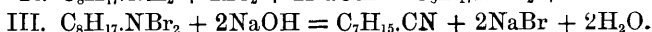
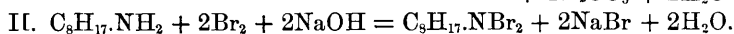
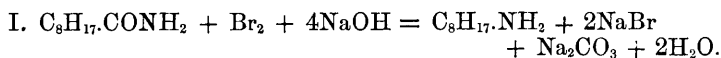
1st Series.				2nd Series.			
				Immersed	10 seconds..	8.8	
					30 „ ..	9.5	
Immersed	1 minute ..	9.5			1 minute ..	9.0	
„	5 minutes..	8.7			5 minutes..	9.0	
„	15 „ ..	8.7			15 „ ..	8.8	

These results are practically identical. As Bechamp has shown, the acid converts the cellulose into a pasty mass, which is entirely dissolved in about five minutes. The acid solution, when poured gradually into a large volume of water, yields very heavy translucent cellules, which are only freed from acid with some difficulty. If the action of the acid is prolonged, the solution is only precipitated when poured into a very large volume of water, and the precipitate does not form instantly. If, however, the solution is poured into alcohol, it is at once precipitated. The precipitate in either case is subjected to prolonged washing with alcohol, and when dried forms a friable substance, slightly soluble in water, and very soluble in a cuprammonium solution; but the latter solution has only about half the rotatory power of a solution of pure cellulose.

C. H. B.

**Conversion of Primary Amines into Nitriles.** By A. W. HOFMANN (*Ber.*, 17, 1920—1921).—In a previous communication (this vol., p. 1114), the author showed that the amide of an acid of the

fatty series may be converted into the nitrile of the next lower member of the series. The occurrence of the amines of the lower homologue in this reaction point to the fact of the intermediate formation of amines. Taking into account the conversion of amines into mono-derivatives of nitrogen bromide (Abstr., 1883, 789), the author thinks the reaction must be looked upon as taking place in three stages:—



L. T. T.

**Trimethylenediamine.** By E. FISCHER and H. KOCH (*Ber.*, **17**, 1799—1801).—The authors have prepared and examined this compound, as it seems to be a suitable starting point for the preparation of the less oxygenised members of the uric acid group.

It was prepared by the action of alcoholic ammonia on trimethylene bromide. Niederist studied the reaction of these bodies on one another, obtaining a number of complicated derivatives (*Monatsh. Chem.*, 1880, 838), but appears to have overlooked the formation of the amine. Trimethylene bromide was mixed with 8 to 9 times its weight of an alcoholic solution of ammonia saturated at 0°, and the mixture was allowed to remain for two or three days in well-closed vessels, at the ordinary temperature. The liquid was then evaporated to dryness, when the hydrobromide of the base was left mixed with bye-products, which appeared similar to those of Niederist, but were not further examined. *Trimethylenediamine*,  $\text{C}_3\text{H}_6(\text{NH}_2)_2$ , is a colourless mobile liquid resembling ethylene and propylene diamines. It distils at 135—136°, and forms a cloud when brought in contact with moist air. When mixed with water, considerable development of heat takes place; when exposed to the atmosphere it absorbs carbonic anhydride, and is converted into the carbonate. It is miscible in all proportions with alcohol, ether, benzene, and chloroform; the anhydrous compound attacks cork and indiarubber readily. The hydrochloride,  $\text{C}_3\text{H}_6(\text{NH}_3\text{Cl})_2$ , crystallises in well-formed colourless prisms, easily soluble in water. The hydrobromide, sulphate, and nitrate are all crystalline, but the two latter exceedingly deliquescent. The platinochloride forms pale red glittering crystals, sparingly soluble in water.

L. T. T.

**Acediamine.** By A. W. HOFMANN (*Ber.*, **17**, 1924—1926).—Strecker showed (*Annalen*, **103**, 328) that when acetamide was acted on by dry hydrochloric acid gas, acediamine,  $\text{C}_2\text{H}_6\text{N}_2$ , was formed. Tawilderow (*Ber.*, **5**, 477) could not obtain acediamine by Strecker's process, and contended that the substance Strecker had obtained was really a mixture of diacetamide hydrochloride, and ammonium chloride. Whilst working at some allied compounds, the author has repeated Strecker's work, with perfectly satisfactory results, obtained a good yield of acediamine, and found none of Tawilderow's difficulties.

In order to assimilate the nomenclature to that he employed for the phenyl-derivative he prepared (*Monatsber. Berl. Akad.*, 1865, 640), the author proposes to substitute the name ethenyldiamine for Strecker's acediamine.

L. T. T.

**Triacetonamine and its Homologues.** By E. FISCHER (*Ber.*, 17, 1788—1799).—In continuation of former communications on this subject (*Abstr.*, 1883, 790 and 1153), the author describes a number of derivatives of triacetonamine which he has investigated.

Triacetonalkamine is best prepared by the reduction of triacetonamine in slightly acid solution by sodium-amalgam. A much better yield is obtained than if the reduction is carried out in alkaline solutions. Triacetonine, already described (*loc. cit.*), is best purified by the help of its hydrobromide; this salt crystallises from boiling water in large prisms. The free base distils at 146—147° under 740 mm. pressure; it is poisonous, and inhalation of its vapour causes giddiness, head-ache, and sickness. It forms an unstable but crystalline hydroxide. The hydriodide and aurochloride are both sparingly soluble in cold water. A solution of the sulphate, when warmed with sodium nitrite, yields *nitrosotriacetonine*,  $C_9H_{16}N.NO$ , which has a strong odour of camphor, and crystallises in yellowish plates, soluble in alcohol, ether, and benzene, very sparingly so in water. When it is boiled with hydrochloric acid, a base is formed which very closely resembles triacetonine. When reduced with zinc and acetic acid, nitrosotriacetonine yields a base which reduces Fehling's solution strongly, and is probably a secondary hydrazine. When heated with methyl iodide, triacetonine yields *methyltriacetonine*, which, however, is better obtained by the action of sulphuric acid on methyltriacetonalkamine at 100°. Methyltriacetonine is a colourless oil, sparingly soluble in water, and easily volatile in a current of steam. Its hydrobromide and hydriodide are easily soluble, and it does not form a hydrate. Its aurochloride crystallises in small, characteristic yellow prisms. It is not attacked by nitrous acid, and is probably a tertiary base.

Triacetonine is an unsaturated compound, and if its hydriodide is heated at 150° with excess of hydriodic acid, the sparingly soluble hydriodide of an iodated base,  $C_9H_{18}NI.HI$ , is formed. Moniodotetramethylpiperidine,  $C_9H_{18}NI$ , is liberated from this hydriodide by the action of potash, and crystallises in colourless plates, easily soluble in alcohol, ether, and chloroform, insoluble in water. It melts at 90°. The hydrochloride is more soluble than the hydriodide. When reduced with sodium-amalgam in aqueous solution, it yields a base very similar in properties to triacetonine. The quantity of this base obtained was too small for the author to determine whether it was tetramethylpiperidine.

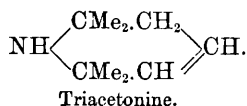
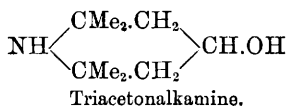
*Pseudo-triacetonalkamine*, described by Heintz (this Journal, 1877, i, 592) as a bye-product in the preparation of triacetonalkamine, was also obtained by the author. He believes, however, that Heintz's formula,  $C_9H_{19}NO$ , is not correct, and that  $C_8H_{18}NO$ , or some multiple thereof, more probably expresses its true composition. It probably is not a simple acetone-base, but is of higher molecular weight. It is

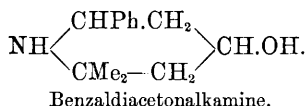
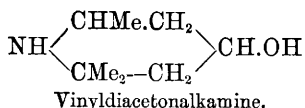
undoubtedly related to the alkamines, as when treated with sulphuric acid at  $100^{\circ}$  it yields *pseudotriacetone*, easily soluble in alcohol, and volatile in a current of steam. It melts at  $128^{\circ}$ , and forms sparingly soluble hydrobromide and hydriodide. It was only obtained in small quantity, and did not yield satisfactory analytical results, but its formula appears to be  $C_8H_{14}N$ .

*Vinyldiacetonamine*,  $C_8H_{15}NO$ , already described by Heintz (this Journal, 1877, ii, 878), is best obtained by the action of paraldehyde on diacetoneamine oxalate. When reduced by sodium-amalgam in acid solution, it yields *vinyldiacetonalkamine*,  $C_8H_{17}NO$ , which melts at  $123^{\circ}$ , and is easily soluble in water and alcohol, very sparingly so in ether. It yields easily soluble salts with mineral acids and with gold and platinum chlorides. Its composition is the same as Wertheim's conhydrine, which it resembles so closely that the author is inclined to look upon the two bases as identical. When heated with concentrated sulphuric acid, vinyldiacetonalkamine yields *vinyldiacetonine*,  $C_8H_{15}N$ , a colourless oil, which may be distilled in a current of steam, and has an odour resembling that of conine. When purified, this base distils at  $137^{\circ}$  under 741 mm. pressure. It is less soluble in boiling than in cold water, and is miscible in all proportions with alcohol, ether, and chloroform. Its hydriodide crystallises in sparingly soluble needles, the hydrochloride and hydrobromide are much more soluble. It forms a crystallisable hydroxide and a characteristic aurochloride. It is converted into a nitrosamine by the action of nitrous acid. It combines with hydriodic acid in a manner similar to triacetone, forming *iodotrimethylpiperidine*,  $C_8H_{16}NI$ ; this crystallises in regular colourless prisms which melt at  $60^{\circ}$ , and are easily soluble in ether, almost insoluble in water.

*Benzaldiacetonamine*,  $C_{13}H_{17}NO$ , was first prepared by Heintz (Abstr., 1879, 54), but the author, having overlooked Heintz's work, redescribed it (this vol., 54) under the name of benzodiacetonamine. He now proposes to revert to Heintz's nomenclature. This compound yields benzaldiacetonalkamine (this vol., p. 54) on reduction, which is converted into the corresponding acetone by the action of strong sulphuric acid. *Benzaldiacetonine*,  $C_{13}H_{17}N$ , has an odour resembling at once that of piperidine and of benzaldehyde. It distils undecomposed, does not solidify at  $-20^{\circ}$ , and is volatile in steam. Its hydrochloride is easily soluble; its hydrobromide and hydriodide very sparingly so. It forms an aurochloride which crystallises in long yellow needles. When heated in acid solution with sodium nitrite, it yields a nitroso-compound.

Heintz gave triacetoneamine the formula  $NH \langle \begin{smallmatrix} CMe_2.CH_2 \\ CMe_2.CH_2 \end{smallmatrix} \rangle CO$ . Accepting this formula as probably correct, the bodies just described will be represented by the following formulæ:—





Latterly the formula  $\text{N} \begin{array}{c} \text{CH : CH} \\ \text{CH : CH} \end{array} \text{N}$  for pyridine has been gaining

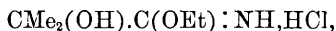
ground. In the formation of acetones from the corresponding alkamines the conditions seem to be very favourable for the bringing about of such a linking of carbon with nitrogen. In every case, however, the imide-group has remained intact, the elements of water having been split off from the carbon nucleus, and thus formed an unsaturated body. There seems, therefore, to be no inclination for the nitrogen in these bodies to unite with the carbon-atom occupying the para-position; and although the case may be different with the less hydrogenised pyridine nucleus, the author considers that, at present at least, the older formula for pyridine should be retained in preference to the new.

L. T. T.

### Imido-ethers from Acetone Cyanhydrin and Allyl Cyanide.

By A. PINNER (*Ber.*, **17**, 2007—2010).—*Chlorobutyrimido-ether hydrochloride*,  $\text{C}_3\text{H}_5\text{Cl.C(OEt):NH.HCl}$ , is prepared by saturating a mixture of equal molecular proportions of allyl cyanide and ethyl alcohol with hydrochloric acid gas. It crystallises in large, thick, colourless prisms. It dissolves readily in water, but the solution soon decomposes with separation of ethyl  $\beta$ -chlorobutyrate. Alcoholic potash appears to convert it into crotonic acid. On long standing, it becomes liquid, and the oil on distillation yields ethyl  $\beta$ -chlorobutyrate and an amide which crystallises in thin colourless needles, melts at  $149\text{--}152^\circ$ , and is readily soluble in alcohol and benzene, probably crotonamide. Ammonia converts the imido-ether hydrochloride into an uncrystallisable amidine hydrochloride.

*Hydroxyisobutyrimido-ether hydrochloride*,



is obtained by the action of hydrochloric acid on a mixture of alcohol and acetone cyanhydrin. It can only be crystallised with difficulty. By treatment with ammonia, it is converted into *hydroxyisobutyramidine hydrochloride*,  $\text{CMe}_2(\text{OH}).\text{C(NH}_2\text{):NH.HCl}$ , which crystallises in large, thick, transparent plates, and is readily soluble in alcohol and water.

By allowing a mixture of cinnamon oil and dry hydrocyanic acid to stand for some weeks, *cinnamaldehyde cyanhydrin*,  $\text{C}_9\text{H}_8\text{O.HCN}$ , is obtained in white granular crystals melting at  $80\text{--}81^\circ$ , readily soluble in alcohol and benzene, sparingly soluble in light petroleum. Hydrochloric acid and alcohol convert it into a crystalline imido-ether.

Cyanbenzin,  $\text{C}_{21}\text{H}_{21}\text{N}_3$ , when pure, crystallises in slender interlaced needles, and melts at  $221^\circ$ .

A. J. G.

**Hydroxy-base of Cyanmethine**,  $\text{C}_6\text{H}_5\text{N}_2\text{O}$ . By R. WOLLNER (*J. pr. Chem.* [2], **29**, 131—134).—The hydroxy-base of cyanmethine

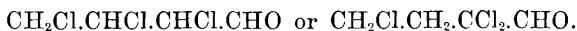


obtained by the action of nitrous acid on cyanmethine in acetic acid solution (Abstr., 1883, 653), differs from the corresponding cyanethine-compound in being very soluble in water. The author has prepared it in a pure state by heating crude cyanmethine with concentrated hydrochloric acid in closed tubes at  $180^{\circ}$ , evaporating, neutralising with soda, and extracting the hydroxy-base with benzene. It forms very soluble crystalline salts with nitric and oxalic acids, and a platinochloride crystallising in plates.

The author has endeavoured to prepare the base  $C_6H_8N_2$ , analogous to cyanconine,  $C_9H_{14}N_2$  (Abstr., 1883, 352). By the action of phosphorus pentachloride on the hydroxy-base an oil containing chlorine was obtained, soluble in ether, alcohol, and benzene, insoluble in water, and nearly insoluble in concentrated hydrochloric acid. With hydrochloric acid gas, this forms a solid compound, probably a hydrochloride, which is insoluble in alcohol and ether, but very hygroscopic; it is decomposed by water into the original oil and hydrochloric acid. On reducing this oil with hydrochloric acid and zinc, neutralising with soda, and distilling with steam, a distillate is obtained having an alkaline reaction, and giving a double salt with mercuric chloride. These compounds are probably analogous to chlorocyanconine and cyanconine, but were obtained in quantities too small for analysis.

On heating the hydroxy-base of cyanmethine with methyl iodide at  $150^{\circ}$ , iodides of methylated ammonias are obtained, chiefly tetramethylammonium iodide, and not a methylated hydroxy-base such as is formed by the action of iodide of methyl on the hydroxy-base of cyanmethine. A. B.

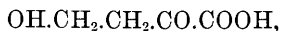
**Compound formed by Addition of Hydrochloric Acid to  $\alpha$ - $\gamma$ -Dichlorocrotonaldehyde.** By K. NATTERER (*Monatsh. Chem.*, 5, 251—265).—In a former communication (Abstr., 1883, 964), the author has shown that  $\alpha$ - $\gamma$ -dichlorocrotonaldehyde unites directly with hydrochloric acid to form a compound isomeric with *butylchloral*, the constitution of which may be represented by either of the two following formulæ:—



The object of this investigation has been to decide between these two formulæ, and the results obtained indicate that this additive compound of hydrochloric acid and  $\alpha$ - $\gamma$ -dichlorocrotonaldehyde is represented by the first of the above formulæ; for if it is boiled with water and barium carbonate, it yields a syrupy compound, which, when dry, forms an amorphous mass, not convertible into erythrol, as would be the case were the constitution represented by the second formula. The substance obtained resembles the carbohydrates, and most probably has the constitution  $OH.CH_2.CH_2.CO.CH_2O$ .

These conclusions find further support in the facts that the *trichlorobutyric acid*, formed by the oxidation of this additive compound, cannot be converted into an unsaturated acid by treatment with zinc-dust and water, or by heating it with an alcoholic solution of potassic iodide. The *trichlorobutyric acid*, which has the constitution,

$\text{CH}_2\text{Cl}.\text{CH}_2.\text{CCl}_2.\text{COOH}$ , appears to form a lactone by replacement of one of the chlorine-atoms, and by long-continued boiling with water is converted into an acid free from chlorine, namely,



which resembles pyrrocemic acid.

P. P. B.

**Formation of Amides from Ammonium Salts.** By N. MENSCHUTKIN (*J. pr. Chem.* [2], **29**, 422—436).—The greater part of this paper has already appeared in a shorter form (*Ber.*, **17**, 846, and this vol., p. 836). The author gives tables containing the rate (that is, the amount formed at the end of one hour) and limit of "amidation" of primary, secondary, and tertiary acids between  $125^\circ$  and  $212.5^\circ$ . The formation of amides follows the same law as that of etherification, and in the following table the values of different acids, compared with formic acid, are given. The temperature of the rate is  $155^\circ$ , and of the limit  $125^\circ$  :—

	Coefficient of etherification.		Coefficient of amidation.	
	Rate.	Limit.	Rate.	Limit.
Primary acids :—				
Formic acid .....	100	100	100	100
Acetic acid .....	71.9	104.8	88.5	143.8
Propionic acid .....	66.7	106.8	88.5	—
Butyric acid.....	53.9	108.2	74.8	149.1
Caproic acid.....	53.6	108.7	83.8	149.5
Phenylacetic acid.....	79.1	115	63.3	—
Secondary acid :—				
Isobutyric acid.....	43.4	108	64.5	149.1
Tertiary acid :—				
Benzoic acid.....	13.9	112.9	1.3	?
Anisic acid .....	8.6	110.4	6.6	?

For the purpose of comparison, the author gives a table (p. 1297) in which various results are shown in relation to the above acids. In Column I are given the results for the affinities of the acids ascertained by the decomposition of acetamide by dilute acids; in Column II the decomposition of methyl acetate by dilute acids; in Column III the value of the investigated acids on salts, the above being Oswald's results. In Column IV is given the thermal effect of the formation of the salts in the solid state by Berthelot.

	I.	II.	III.	IV.
Formic acid .....	100	100	100	100
Acetic acid .....	48·4	51·5	34·1	80·9
Propionic acid .....	—	48·3	26·6	—
Butyric acid .....	—	47·9	25·1	76·7
Isobutyric acid .....	—	45·4	23·6	—
Isovalerianic acid .....	—	—	—	64·2

In all the above reactions, the acids investigated show the same relations. In all the columns similar changes in the composition or isomerism of the acids show similar changes in the figures, so that in all the reactions the same series are obtained. A. B.

**Influence of Temperature on the Rate of Certain Reactions.** By N. MENSCHUTKIN (*J. pr. Chem.* [2], 29, 437—447).—In this paper are given the conclusions derived from the author's investigations on the formation of ethyl acetate from acetic acid and ethyl alcohol, acetamide from acetic acid and ammonia, and acetanilide from acetic acid and aniline. These reactions are not simple as are the combination of two compounds, or the decomposition of one compound into two, but are double decompositions and the more complicated as they are reciprocal. The estimations are not those of the rate of formation or decomposition, but the differential of the rate of the two reactions. Disregarding this disadvantage, it is found that the influence of temperature on the increase in the rate of the reaction is regular. The method of investigation has been to warm molecular weights of the substance for an hour at various temperatures, and then estimate the quantities of ethereal salt, anilide, or amide, as the case might be, which were formed.

The influence of the temperature on the increase of the rate of formation of ethyl acetate is given in the following table. In the first column is given the temperature of the experiment; in the second the percentage of ethyl acetate formed; and in the third the difference in the increase, usually between 10°.

Temperature.	Amount of ethyl acetate formed.	Difference.
90°	7·50	6·0
102	13·50	5·52
112	19·02	5·76
122	24·78	7·82
132	32·60	8·05
142	40·65	6·17
152	46·82	6·17
162	52·99	4·46
172	57·45	3·54
182·5	60·99	2·99
212·5	63·98	—

In the formation of the ethereal salt, the rate increases with the rise of temperature throughout, but the amount of increase has a maximum and then diminishes. This maximum lies between  $125^{\circ}$  and  $145^{\circ}$ , when the formation is about half completed. The rate at  $212.5^{\circ}$  approaches the limit of the reaction (66.6 per cent.). The author represents these reactions by means of curves, of which the abscissa is the temperature and the ordinate the percentage of ethereal salt, anilide, or amide formed. The curve of the rate of formation of ethyl acetate has the appearance of an elongated letter S.

The influence of temperature in the formation of acetanilide is shown in the following table :—

Temperature.	Amount of acetanilide formed.	Difference.
$82^{\circ}$	6.08	2.42
90	8.50	6.09
102	14.59	6.92
112	21.51	9.2
122	30.71	9.2
132	39.91	7.74
142	47.65	7.84
152	55.49	6.08
162	61.57	4.82
172	66.39	2.48
182.5	68.87	3.32
212.5	72.19	—

In this and in the preceding case, the commencement of the formation begins at the ordinary temperature, but the amount is small. The maximum of the increase in the rate is between  $122^{\circ}$  and  $132^{\circ}$ , and in this case it is again half completed. The curve in these reactions is of the same form as the ethyl acetate curve.

Finally, in the case of acetamide, the following results have been obtained :—

Temperature.	Amount of acetamide formed.	Difference.
$100^{\circ}$	0	1.27
110	1.27	3.14
121	4.41	4.61
130	9.02	12.34
140	21.36	15.60
150	36.96	—
152	40.66	—
155	50.90	21.71
160	58.67	13.66
172	72.33	5.98
182.5	78.31	4.52
212.5	82.83	—

In this increase, the maximum of increase in rate is sharper and much greater than in the two former cases. At  $212.5$  the rate is almost equal to the limit (84.0 per cent.). The curve is like an

upright S, and the maximum in the increase in the rate is about half of the total decomposition.

In these reciprocal reactions the limit depends on the rate of both reactions being the same. Berthelot has shown that temperature has no influence on the limit in the cases of different systems of alcohols and acids, and the author has confirmed this. In the formation of acetanilide, the author shows that a decrease in the limit takes place by rise of temperature, and in the formation of acetamide, an increase. The following table shows this:—

Acetamide.		Acetanilide.	
Temperature.	Limit.	Temperature.	Limit.
100°	85·05 per cent.		—
125	83·11	125°	75·10 per cent.
135	82·39	140	78·18
145	81·22	155	81·46
155	79·68	182·5	82·82
182·5	78·85	212·5	84·04
212·5	77·75		—

Probably in these cases the limit may become constant at higher temperatures.

In these reactions, the differences are small as compared with the differences in the chemical properties of the substances, and it seems probable that the above experiments show the general character of the influence of temperature in such reactions, which imply double decomposition.

A. B.

**Acids contained in Beeswax.** By F. NAFZGER (*Annalen*, **224**, 225—258).—Brodie's formula for cerotic acid (*Annalen*, **67**, 180; **71**, 144),  $C_{27}H_{54}O_2$  has been called in question by Heintz (*J. pr. Chem.*, **66**, 1) and others. Schalfejeff (*Ber.*, **9**, 278 and 1688) denies that it is a homogeneous product, and states that it is a mixture of the acid  $C_{34}H_{68}O_2$ , melting at 91°, with other acids of the same series.

The author finds that the cerine of beeswax consists chiefly of free cerotic acid, melting at 78·5°, mixed with a small quantity of acids of the oleic series. By fractional precipitation of the alcoholic solution with magnesium acetate, a small quantity of an acid melting at 89° was isolated. It has the formula  $C_{30}H_{60}O_2$  or  $C_{31}H_{62}O_2$ .

Analyses of cerotic acid and its lead and silver salts failed to decide whether the acid has the composition  $C_{26}H_{52}O_2$  or  $C_{27}H_{54}O_2$ . They prove, however, that this acid is not identical with the lignoceric acid of Hell and Hermann (*Abstr.*, 1881, 249).

Myricin is chiefly composed of myricyl palmitate and the myricyl salt of an acid of the oleic series.

W. C. W.

**Action of Bromine on Levulinic Acid ( $\beta$ -Acetopropionic Acid).** By C. HELL and E. A. KEHRER (*Ber.*, **17**, 1981—1984)—*Dibromlevulinic acid*,  $C_5H_6Br_2O_3$ , is obtained by gradually adding bromine to an ethereal solution of levulinic acid, the reaction being very vigorous. It is also formed by adding bromine to an aqueous solution of levu-

linic acid and allowing the mixture to stand for some days, best in sunlight. It crystallises in tufts of needles, or in thick, apparently rhombic, prisms, melts at 112—113°, and is decomposed at 130—140°. It is readily soluble in ether, alcohol, acetic acid, ethyl acetate, and acetone, sparingly soluble in cold water, chloroform, and benzene, practically insoluble in light petroleum. It is not decomposed by cold water, whilst hot water decomposes it with elimination of all its bromine as hydrobromic acid, and an amount of carbonic anhydride equal to a little less than one-fifth of the carbon present as COOH; the other decomposition-products have not been isolated. The bromine-derivative was also prepared from synthetical  $\beta$ -acetopropionic acid, and agreed in all particulars with that above described, confirming the statement of Conrad (Abstr., 1879, 453) and Tollens (*ibid.*, 523), as to the identity of levulinic and  $\beta$ -acetopropionic acid.

A. J. G.

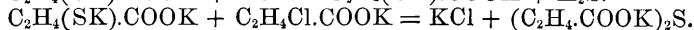
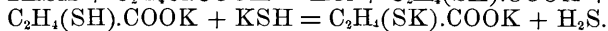
**Preparation of Glyoxal Derivatives from Trichlorlactic Acid.**

By A. PINNER (*Ber.*, 17, 1997—2002).—On heating a mixture of trichlorlactic acid and carbamide dissolved in a little water, on the water-bath for 10—12 hours, acetylene-carbamide is formed. If the water be omitted, dichlorovinyl-carbamide is obtained in addition. By the action of excess of ammonia on trichlorlactic acid, glycosine is formed, one of the nitrogenous bases obtained by Debus by action of ammonia on glyoxal. A mixture of trichlorlactic acid, hydroxylamine hydrochloride, and sodium carbonate yields glyoxime. Phenylhydrazine acting on sodium trichlorlactate converts it into the compound  $C_{14}H_{14}N_4$ , previously obtained by E. Fischer (this vol., p. 1151) from glyoxal and phenylhydrazine. Sodium amalgam converts trichlorlactic acid into a crystalline chlorinated acid, probably monochlorlactic acid.

A. J. G.

**Thiolactic and Thiodilactylic Acids.** By J. M. LOVÉN (*J. pr. Chem.* [2], 29, 366—378).—An acid of the supposed formula  $C_2H_4(SH).COOH$ , is described by Schacht (*Annalen*, 129, 1), and Böttiger (Abstr., 1876, 624); the same chemists also briefly mention a thiodilactylic acid, but the author considering it very doubtful whether the acids described by them were really those in question, has subjected these acids to a detailed investigation.

*Action of  $\alpha$ -Chloropropionic acid on Potassium Sulphhydrate.*—When pure chloropropionic acid is gradually added to a concentrated solution of potassium sulphhydrate, sulphuretted hydrogen is evolved, and potassium chloride, thiolactate, and thiodilactylate are formed according to the equations:—



The thiodilactylate was precipitated by means of barium chloride, and the thiolactic acid obtained from the filtrate by acidulating with sulphuric acid and shaking with ether.

$\alpha$ -Thiolactic acid,  $CHMe(SH).COOH$ , may be prepared more easily by saturating an aqueous solution of pyruvic acid with sulphuretted

hydrogen at a gentle heat, strong hydrochloric acid and zinc are then added; on cooling, the thiolactic acid is extracted with ether. The acid is a colourless oily liquid of unpleasant odour, and miscible with water and alcohol in all proportions. Ferric chloride gives a transient indigo-blue colour, after which alkalis give an intense purple-red coloration which gradually disappears in contact with the air. Excess of ferric chloride converts it into dithiolactylic acid. Cupric salts added in excess produce a deep-violet solution (distinction from  $\beta$ -thiolactic and thioglycollic acids, which give precipitates). A number of salts derived from thiolactic acid are described; those metals which are precipitated from an acid solution by sulphuretted hydrogen form acid compounds, by displacement of the hydrogen which is combined with sulphur, of the type  $C_2H_4(SR).COOH$ . Ethylic thiolactate, prepared by heating a mixture of thiolactic acid with alcohol and a little sulphuric acid, is a mobile liquid of intensely disagreeable odour, and only slightly soluble in water; with solutions of the heavy metals, it behaves like mercaptan; thus with copper it forms a compound  $[C_2H_4(COOEt)S]_2Cu_2$ .

*Dithiodilactylic acid*,  $(C_2H_4.COOH)_2S_2$ , is prepared by the oxidation of thiolactic acid with iodine or ferric chloride; it crystallises in shining needles or hard cakes, which melt at  $142^\circ$ , and are sparingly soluble in cold but readily in hot water, alcohol, or ether. It gives no reactions with either copper or iron salts; zinc and hydrochloric acid convert it into thiolactic acid, which is thus most readily obtained in a pure state. The author regards it as almost beyond doubt that the acid prepared by Schacht and Böttinger was really dithiolactylic acid, the percentage composition being but slightly different from that of thiolactic acid.

*Thiodilactylic acid*,  $(C_2H_4.COOH)_2S$ .—As already mentioned, this acid is obtained as a bye-product in the preparation of thiolactic acid. It is formed as the principal product by the action of potassium  $\alpha$ -chloropropionate either on potassium sulphide or on basic potassium thiolactate. The free acid is obtained from its barium salt by acidulation with sulphuric acid; it crystallises in large well-formed monoclinic prisms melting at  $125^\circ$ . The acid is very soluble in water, alcohol, and ether; it suffers no change from contact with the air, and is not acted on by nascent hydrogen or sulphuretted hydrogen.

*$\beta$ -Thiolactic acid* (thiohydraerylic acid),  $CH_2(SH).CH_2.COOH$ , is obtained by the action of  $\beta$ -iodopropionic acid on potassium sulphhydrate; there is no second acid formed in this reaction. It is best prepared in a state of purity by reducing  $\beta$ -dithiodilactylic acid. It is a colourless liquid of a disagreeable, penetrating odour, differing from that of  $\alpha$ -thiolactic acid; with the latter acid, however, it agrees in most respects, but is more readily oxidised in contact with the air to  $\beta$ -dithiolactylic acid, and with cupric salts gives a light-violet precipitate, which soon turns to a dirty green colour. The compounds with the heavy metals are similar to those of  $\alpha$ -thiolactic acid, thus:  $[CH_2(COOH).CH_2.S]_2Hg$ .

*$\beta$ -Dithiodilactylic acid*,  $[CH_2(COOH).CH_2]_2S_2$ , is obtained by treating crude thiohydraerylic acid with ferric chloride as long as a transient blue colour is produced, a voluminous crystalline precipitate is obtained,

which is washed with cold and recrystallised from hot water. The acid forms thin silvery plates almost insoluble in cold water. It is reduced to thiohydracrylic acid by nascent hydrogen.

P. F. F.

**Action of Ethyl Dibromosuccinate on Ethyl Malonate.** By W. H. PERKIN, jun. (*Ber.*, 17, 1652—1658).—Sodium (4 grams) is dissolved in absolute alcohol (50 grams), ethyl malonate (14 grams) added, and then gradually an alcoholic solution of ethyl dibromosuccinate, the whole being well cooled after each addition. The product is heated on a water-bath until it becomes neutral, diluted with water, and the oil extracted with ether. The *ethylic trimethylenetetra-carboxylate*,

$(\text{COOEt})_2\text{C} \begin{array}{c} \text{CH.COOEt} \\ | \\ \text{CH.COOEt} \end{array}$ , obtained, is a very thick, colourless oil of

agreeable odour; it boils at 245—247°, and does not solidify in a freezing mixture. In order to obtain the free acid, the ethyl salt is boiled with an excess of soda solution, the whole evaporated nearly to dryness, acidulated with dilute sulphuric acid, and extracted with ether. *Trimethylenetetra-carboxylic acid* forms a hard, colourless crystalline mass, and melts at 95—100° with evolution of carbonic anhydride. It is a strong acid, dissolves readily in water, ether, alcohol, and acetone, sparingly in light petroleum, benzene, and toluene. The silver salt,  $\text{C}_7\text{H}_2\text{O}_8\text{Ag}_4$ , is obtained by precipitation from the ammonium salt as a white amorphous precipitate; it decomposes suddenly on heating. The ammonium salt is not precipitated by copper sulphate, whilst with barium chloride it yields a white gelatinous precipitate very sparingly soluble in water. The *calcium salt*,  $\text{C}_7\text{H}_2\text{O}_8\text{Ca}_3\cdot\text{H}_2\text{O}$ , separates on warming a solution of the ammonium salt to which calcium chloride has been added; it is much more soluble in cold than in hot water. When trimethylenetetra-carboxylic acid is heated at 190—200°, carbonic anhydride is evolved, and *trimethylenetricarboxylic acid*,

$\text{COOH.CH} \begin{array}{c} \text{CH.COOH} \\ | \\ \text{CH.COOH} \end{array}$ , is obtained as in an oil. When

purified it is crystalline, melts at about 145—150°, dissolves readily in water, alcohol, and acetone, and sparingly in light petroleum, benzene, carbon bisulphide, and chloroform. When it is heated, it first gives off water, partially carbonises and yields a small quantity of distillate; this solidifies on cooling, is sparingly soluble in ether, and is probably the anhydride of the acid. The *silver salt*,  $\text{C}_6\text{H}_3\text{O}_6\text{Ag}_3$ , forms a white granular precipitate, and does not explode when heated. The ammonium salt yields a bright-green sparingly soluble precipitate with cupric sulphate, and very sparingly soluble white precipitates with barium chloride and lead acetate, whilst with calcium chloride no precipitate is formed except on warming, the calcium salt being much more soluble in cold than in hot water, and apparently almost insoluble in boiling water. The trimethylenetricarboxylic acid is isomeric with the acid described by Conrad and Guthzeit (this vol., p. 991), with aconitic and carboxylglutaconic acids, and is perhaps identical with Baeyer's aceconitic acid (*Annalen*, 135, 206).



At the end of the paper, a table is given containing all the trimethylene- and tetramethylene-derivatives hitherto prepared.

A. K. M.

**Homologues of Glycidic Acid.** By MELIKOFF (*Bull. Soc. Chim.*, **41**, 311).—When crotonic acid is acted on by hypochlorous acid, *chloroxybutyric acid* is obtained which melts at 62–63°, and this when treated with alcoholic potash gives the potassium salt of

*propyleneoxycarboxylic acid*,  $\text{O} \begin{array}{l} \text{CHMe} \\ | \\ \text{CH.COOK} \end{array} \frac{1}{2} \text{H}_2\text{O}$ , which crystallises

in small prisms. The silver salt likewise crystallises in prisms, and its aqueous solution forms a silver mirror when boiled. The acid melts at 84° and evolves suffocating vapours; it forms additive compounds, and combines with hydrochloric acid, evolving heat and producing an isomeric chloroxybutyric acid, melting at 85°. The acid is distinguished from glycidic acid by absorbing water when exposed to the air, with formation of glyceric acid. When heated with water at 120°, *propyleneglycolcarboxylic acid* is obtained, of which the barium and silver salts were examined. Treated with ammonia, the acid yields *amidoxybutyric acid*, which crystallises in prisms and combines with both acids and bases. Metacrylic acid is converted by hypochlorous acid into *chlorisobutyric acid*; this melts at 106–107°, and boils at 230–235° with partial decomposition. It is decomposed by alcoholic potash, yielding *metoxyacrylic acid*,  $\text{C}_4\text{H}_5\text{O}_3, \frac{1}{2} \text{H}_2\text{O}$ . The potassium salt of this acid crystallises in prismatic plates, and the silver salt in needles. The free acid is a viscous liquid, which combines with hydrochloric acid, forming *chloroxyisobutyric acid*. The acids containing the ethylene oxide residue are distinguished by combining directly with other bodies.

W. R. D.

**Isomerism of Fumaric and Maleic Acids.** By PÉTRIEFF (*Bull. Soc. Chim.*, **41**, 309).—The additive compounds of fumaric and maleic acids are distinguished by different boiling and fusing points; when they are saponified, fumaric acid is formed. The action of chlorine on fumaric acid gives rise to dichlorosuccinic and trichloroacetic acids. Under the same conditions, maleic acid also forms a dichlorosuccinic acid which differs in solubility and fusing point from that obtained from fumaric acid. Fumaric acid combines with hypochlorous acid, forming a liquid which yields inactive maleic acid when reduced by sodium-amalgam. Maleic acid when treated in the same way also gives inactive maleic acid together with an acid of the formula  $\text{C}_4\text{H}_4\text{O}_5$ , which is probably oxymaleic acid, and an acid liquid having the composition of maleic acid, but which, when heated, is decomposed into carbonic anhydride and a substance having the formula  $\text{C}_6\text{H}_{10}\text{O}_5$ . By the action of zinc ethyl on the neutral ether of fumaric acid ethylsuccinic acid was obtained. The author considers that the formula for fumaric acid which has been proposed by Fittig, accurately represents the constitution of the acid, but does not admit the formula for maleic acid which has been suggested by the same chemist.

W. R. D.

**Action of Hydroxylamine on Meconic, Comenic, and Pyromeconic Acids.** By E. ODERNHIMER (*Ber.*, **17**, 2081—2088).—By the action of hydroxylamine hydrochloride on an alcoholic solution of meconic acid, there is obtained a compound of the formula  $C_7H_5O_7N + H_2O$ . It crystallises in colourless rosettes of small needles, readily soluble in water, sparingly soluble in alcohol, ether, and chloroform, insoluble in light petroleum; it decomposes suddenly when heated to about  $190^\circ$ . Heated with strong hydrochloric acid hydroxylamine is separated. The aqueous solution has a strongly acid reaction and reduces Fehling's solution at the ordinary temperature. With both the acid and salts, ferric chloride gives a characteristic red coloration similar to that produced by meconic acid. Two silver salts were obtained, the first a yellow salt by the addition of silver nitrate to a neutral solution of the ammonium salt, it is very unstable; on adding ammonia a silver mirror is deposited; the second is a white salt,  $C_7H_5O_7NAg_2 + H_2O$ , formed on adding silver nitrate to a cold aqueous solution of the free acid; it is sparingly soluble in hot water, insoluble in alcohol. The normal calcium salt,  $C_7H_5O_7NCa + 4H_2O$ , forms thin transparent plates. The acid salt,  $(C_7H_5O_7N)_2Ca + 2H_2O$ , is obtained by addition of calcium chloride to the free acid; it crystallises in white needles. The sodium salt,  $C_7H_5O_7NNa$ , is crystalline and insoluble in alcohol. The barium salt,  $(C_7H_5O_7N)_2Ba + 10H_2O$ , crystallises in feathery groups of needles. These results show that there is only a single oxygen-atom in meconic acid capable of entering into reaction with hydroxylamine, and renders it very probable that meconic acid is a ketonic acid of the formula  $C_4HO(CO)(OH).COOH$ , the isonitroso-derivative having the formula  $C_4HO(C:NOH)(OH).COOH$ . The author's experiments with hydroxylamine hydrochloride and comenic and pyromeconic acids yielded negative results. The author has investigated the action of hydroxylamine on dehydracetic acid, and obtained results confirming those of Perkin and Bernhart (this vol., p. 1121).

A. J. G.

**Action of Hydroxylamine and Ethylamine on Comanic Acid.** By H. OST (*J. pr. Chem.* [2], **29**, 378—380).—This is a preliminary note published in consequence of the appearance of a paper by V. Meyer (*Abstr.*, this vol., p. 993), on the action of hydroxylamine on chelidonic and meconic acids. On mixing equivalent weights of comanic acid,  $C_5H_3O_2.COOH$ , hydroxylamine hydrochloride, and sodium carbonate with water, and heating, the whole dissolves, but soon a body separates having the composition of an oximido-comanic acid,  $C_5H_3O(NOH).COOH$ . This substance, however, does not behave like an oximido-compound, for the nitrogen is not loosely combined, and when heated with fuming hydrochloric acid no hydroxylamine is eliminated, but at  $200^\circ$  carbonic anhydride is evolved with formation of a compound  $C_5H_5NO_2$ . Tin and hydrochloric acid convert the oximido-compound into  $\beta$ -hydroxypicolinic acid, which is also readily formed from comanic acid and ammonia. It would thus appear that the hydroxylamine acts similarly to ammonia, and that the above compound is a dihydroxypyridinecarboxylic acid. Ethylamine converts comanic acid into an acid,  $C_5H_5NO_3 +$

$\frac{1}{2}\text{H}_2\text{O}$ , which appears to be ethylpyridinehydroxycarboxylic acid,  $\text{C}_5\text{H}_2\text{EtN}(\text{OH})\cdot\text{COOH}$ . Similarly comenic acid and ethylamine give  $\text{C}_8\text{H}_9\text{NO}_4$ , which is probably dihydroxy-ethylpyridinecarboxylic acid, whilst aniline and comenic acid give a corresponding phenyl-com-pound,  $\text{C}_{12}\text{H}_9\text{NO}_4$ .  
P. F. F.

**Decomposition of Optically Inactive Compounds.** By E. JUNGFLEISCH (*Bull. Soc. Chim.*, **41**, 222—226).—The author considers that the separation or non-separation of inactive compounds by "compensation" is determined by the relative solubility of the inactive compound, and of the two compounds into which it is capable of being separated. If the original compound is less soluble than either of the compounds of which it is constituted, no separation is effected by crystallisation; but if either of the constituent compounds is less soluble than the original compound, separation occurs under certain conditions when crystallisation is attempted. This being the case, the result will vary at different temperatures; thus it has been noticed that sodium potassium tartrate can be crystallised without decomposition near  $0^\circ$ , the salt at this temperature being less soluble than either the dextrorotatory or levorotatory salts which compose it. The unequal solubility of the two products of the decomposition also appears to be an important factor in producing the result. This has been investigated in the case of sodium ammonium racemate, a process for the separation of which into dextrorotatory and levorotatory sodium ammonium tartrates has been devised by the author, and fully described in a previous Abstract (*Abstr.*, 1882, 602). As the result of a number of experiments, it is noticed that in the first crystallisation the dextrorotatory salt is deposited in greater quantity than the levorotatory, but in the second crystallisation the reverse is the case. Further, a supersaturated solution of ammonium sodium racemate, from which the dextrorotatory and levorotatory salts have been, as far as possible, separated by crystallisation, when examined by the polariscope is feebly levorotatory, and on the addition of boric acid becomes markedly so. These facts indicate the greater solubility of the levorotatory salt in the saline liquid. The decomposition of cinchonine racemate into dextrorotatory and levorotatory cinchonine tartrate, and of cinchonine paraphenyglycollate into the two active cinchonine phenyglycollates, may be explained by the wide difference in the solubilities of the constituent salts. The behaviour of paracamphoric acid also supports this view. When a hot concentrated solution of this acid is cooled and fractionally crystallised, the crystals which separate between  $80^\circ$  and  $40^\circ$  are strongly levorotatory, whilst those formed below  $40^\circ$  are dextrorotatory. By recrystallising these fractions they become more and more strongly levorotatory. In this way crystals were obtained containing 75 per cent. of the levorotatory acid. When a solution of paracamphoric acid is crystallised, and the crystals allowed to remain in the cold in contact with the mother-liquor, they are reconverted into the original acid. The difference in the solubility of the dextro- and levorotatory camphoric acids can be still further increased by the addition of acetic acid.

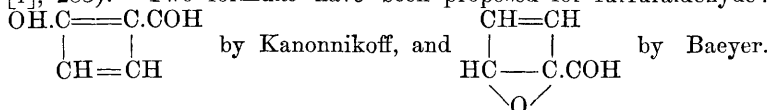
W. R. D.

**Synthesis of Tartaric Glucoside.** By A. GUYARD (*Bull. Soc. Chim.*, **41**, 291).—When tartaric anhydride is added to glucose which has been heated to incipient fusion, water is given off, and a white substance remains which is entirely soluble in water. The aqueous solution is unaltered by prolonged ebullition, and neither tartaric acid nor glucose can be detected by the ordinary reactions. When the solution is boiled with a dilute mineral acid, tartaric acid and glucose are regenerated. W. R. D.

**Occurrence of Citric Acid in the Seeds of Leguminosæ.** By H. RITTHAUSEN (*J. pr. Chem.* [2], **29**, 357—359).—Malic, oxalic, and citric acids have been proved to exist in the seed of the yellow lupin (*Lup. luteus*) (Beyer, Abstr., 1872, 519; *J. pr. Chem.* [2], **2**, 339), by the author and others. He has since found citric acid in the seeds of *Vicia sativa*, *V. faba*, *Pisum sativum*, and *phaseolus*. The powdered seeds were extracted with water, acidified with hydrochloric acid, the solution neutralised with potash or soda and concentrated; the residue, after filtration, was treated with basic lead acetate; the precipitate was decomposed with sulphuretted hydrogen in the usual way, and the clear liquid rendered strongly alkaline with lime-water. The precipitate, consisting chiefly of calcium phosphate, was filtered off and the solution boiled to precipitate the calcium citrate, from which the citric acid was prepared by decomposition with sulphuric acid. P. F. F.

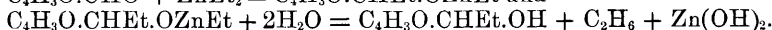
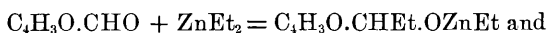
**Furfuraldehyde.** By A. GUYARD (*Bull. Soc. Chim.*, **41**, 289—291).—When paper steeped in aniline acetate is immersed in a liquid containing furfuraldehyde, a magnificent rose-red colour is produced. Furfuraldehyde is contained in pyroligneous acid, and it is to this substance that acetic acid, prepared from pyroligneous acid, owes the peculiar odour which renders it unfit for the preparation of vinegar. The furfuraldehyde can be removed from pyroligneous acid, from which the tar has been separated, by agitating it with benzene. The compound remains when the benzene is evaporated. The acid can be purified by distillation. W. R. D.

**Constitution of Furfuraldehyde.** By A. PAWLINOFF and G. WAGNER (*Ber.*, **17**, 1967—1969).—One of the authors has recently shown that aldehydes combine directly with zinc alkyls forming the alkylates of secondary alcohols (*Jour. Russ. Chem. Soc.*, 1884, [i], 283). Two formulæ have been proposed for furfuraldehyde:



The action of zinc ethyl gives a means of investigating the question, as if a hydroxyl-group be present it will attack that as well as the aldehyde-group. The authors' results show that the second oxygen atom is not present as hydroxyl, the product of the reaction yielding, on treatment with water, *ethyl furfuryl carbinol*,  $\text{C}_4\text{H}_3\text{O.CHEt.OH}$ .

Its formation is represented by the equations—



It is a colourless viscid liquid of agreeable aromatic odour, and is moderately soluble in water. It boils without decomposition at  $180^\circ$  under 749 mm. pressure, has a sp. gr. of 1.066 at  $0^\circ$ , and of 1.053 at  $15.5^\circ$  (water at  $0^\circ = 1$ ). Acetic anhydride exerts a dehydrating influence on it, converting it into a mixture of hydrocarbons.

A. J. G.

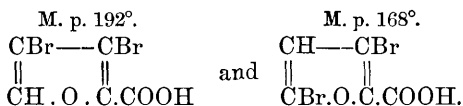
**Substitution-derivatives of Pyromucic Acid.** By H. B. HILL and C. R. SANGER (*Ber.*, 17, 1759—1764).—Tönnies described (*Abstr.*, 1878, 785) a dibromopyromucic acid (m. p.  $184$ — $186^\circ$ ), obtained by the action of potash on pyromucic acid tetrabromide, but did not give the details of its preparation.

If an alcoholic solution of the tetrabromide is poured slowly into excess of strong alcoholic soda, care being taken to prevent any great rise in temperature, the sodium salts of two dibromopyromucic acids are obtained. These salts are sparingly soluble in alcohol, and the acids can be easily separated by means of the difference in the solubilities of their calcium salts. The more soluble salt yields an acid melting at  $192^\circ$ ; the less soluble one melting at  $168^\circ$ . The former acid crystallises in flat needles, easily soluble in boiling water, in alcohol, ether, boiling benzene or chloroform, very sparingly in carbon bisulphide and light petroleum. When heated with dilute nitric acid (1 : 5) it dissolves with evolution of carbonic anhydride, and the solution contains a mixture of mucobromic and dibromomaleïc acids. This acid is undoubtedly the same as that obtained by Tönnies. By the action of bromine-water on his acid, Tönnies obtained an easily soluble substance melting at  $88^\circ$ , which he believed to be the aldehyde of dibromofumaric acid. The authors have obtained a compound having the same properties, but only in very small quantity. When the acid is suspended in water, and bromine vapour is passed into the liquid by means of a current of air, tetrabromotetraphenol (tetrabromofurfuran),  $\text{C}_4\text{Br}_4\text{O}$ , melting at  $64$ — $65^\circ$ , is formed, according to the equation  $\text{C}_5\text{H}_2\text{Br}_2\text{O}_3 + 2\text{Br}_2 = \text{C}_4\text{Br}_4\text{O} + \text{CO}_2 + 2\text{HBr}$ .

The second dibromopyromucic acid, melting at  $168^\circ$ , can be more easily prepared by the action of bromine (2 mols.) on dry pyromucic acid. The resulting mixture of the acid and its dibromide is treated with water to decompose the bromide, and the acid purified by means of its calcium salt: some dibromomaleïc acid is always formed in the reaction. This dibromopyromucic acid is easily soluble in boiling water, in alcohol, and ether, in boiling benzene or chloroform, sparingly in carbon bisulphide. When heated with dilute nitric acid, it is oxidised and yields monobromofumaric acid,  $\text{C}_4\text{H}_3\text{BrO}_4$ . When bromine is allowed to act on the acid suspended in water, monobromomaleïc bromide,  $\text{C}_4\text{HBr}_3\text{O}_3$ , is formed. This last reaction seems to proceed most regularly when the bromine is added quickly. Monobromomaleïc bromide crystallises in long white needles melting at  $55^\circ$ . It is slowly acted on by boiling water, and yields, apparently, a mixture of monobromofumaric, monobromomaleïc, and dibromosuc-

cinic acids. The other usual solvents dissolve it readily. When decomposed with potash, it yields monobromomaleic acid.

Judging from their oxidation-products, the authors believe that the two acids may best be represented by the formulæ



and therefore names them respectively  $\beta\gamma$ - and  $\beta\delta$ -dibromopyromucic acid.

When treated in ammoniacal solution with zinc-dust, both acids yield  $\beta$ -monobromopyromucic acid melting at  $128$ — $129^{\circ}$ . This acid crystallises in needles, and is easily soluble in the usual solvents. When boiled with dilute sulphuric acid, it yields monobromofumaric acid melting at  $176$ — $177^{\circ}$ .

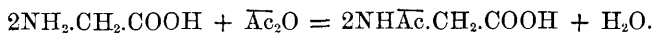
$\delta$ -Monobromopyromucic acid melting at  $183$ — $184^{\circ}$  combines easily with bromine to form an additive product, which melts at  $170^{\circ}$  with decomposition; this, when treated with alcoholic potash, readily yields tribromopyromucic acid, crystallising in small tufts of needles melting at  $218$ — $219^{\circ}$ . It is sparingly soluble in boiling water, easily in ether or alcohol, and almost insoluble in light petroleum and carbon bisulphide. When oxidised by moderately strong nitric acid ( $1:2$ ), it yields dibromomaleic acid: bromine-water converts it into tetrabromotetra-phenol, together with a small quantity of dibromomaleic acid.

L. T. T.

**Optical Behaviour of certain Amido-acids.** By E. SCHULZE and E. BOSSHARD (*Ber.*, **17**, 1610).—The amido-acids obtained on heating conglutin with hydrochloric acid are optically active; leucine dissolved in hydrochloric is dextrorotatory, and tyrosine lævorotatory; glutaminic acid, under the same conditions, is also dextrorotatory. The tyrosine, leucine, and glutamic acid, which are obtained by the action of baryta-water on conglutin, are however optically inactive; this applies to both acid and alkaline solutions, and in the case of the two latter substances has also been proved for aqueous solutions. Differences of solubility of the active and inactive amido-acids have also been observed.

A. K. M.

**Aceturic Acid (Acetylglucocoll).** By T. CURTIUS (*Ber.*, **17**, 1663—1674).—The author prepares aceturic acid by boiling glycocine (40 grams), dried, and finely powdered, with acetic anhydride (60 grams) and benzene (250 grams) for four hours, the flask being frequently shaken to prevent the glycocine from caking. The benzene is distilled off, the residue dissolved in hot alcohol, and the solution decolourised by animal charcoal. The reaction is nearly quantitative, and may be expressed thus:



The yield is not so good when finely powdered dry glycocine-silver (30 grams) is boiled with acetic chloride (16 grams) and benzene (200 grams), as in Kraut and Hartmann's method (*Zeitschr. f.*

*Chem.*, 1868, 79). In this reaction, however, other compounds are formed, as in the reaction between benzoic chloride and glycocine-silver (Abstr., 1883, 337); the analogue of the acid,  $C_{10}H_{11}N_3O_4$ , has, for instance, been obtained, and forms a microcrystalline powder melting above  $260^\circ$  after first blackening; it is decomposed by boiling with mineral acids, with formation of acetic acid, glycocine, and a substance which yields ammonia when heated with aqueous alkalis. Aceturic acid separates from a hot saturated aqueous solution in colourless lanceolate crystals radiating from a common centre, and from a dilute solution, by evaporation in a vacuum, in small lustrous diaxial crystals; it melts at  $206^\circ$ . A litre of water at  $15^\circ$  dissolves 27 grams of the acid; it is moderately soluble in cold, readily in hot alcohol, and very readily in boiling water, but is insoluble in boiling ether, benzene, and toluene; it is only sparingly soluble in hot glacial acetic acid or acetone. Aceturic acid gives a red colour with ferric chloride and a deep blue colour with phenol and hypochlorites, and is decomposed by acids and alkalis much more readily than hippuric acid. It combines with hydrochloric and sulphuric acids, but the salts obtained are readily decomposed by water; with bases, however, it forms stable salts, most of which are very soluble in water. The *silver salt*,  $NH\dot{A}c.CH_2.COOAg$ , is moderately soluble in cold, very readily in hot water, and insoluble in absolute alcohol; the *ammonium salt*,  $NH\dot{A}c.CH_2.COONH_4.H_2O$ , crystallises in glistening needles or large plates which effloresce over sulphuric acid; when boiled with water or alcohol, it splits up into free acid and ammonia; it is moderately soluble in cold, very readily in hot water, less so in hot alcohol. The *barium salt*,  $(NH\dot{A}c.CH_2.COO)_2Ba.5H_2O$ , crystallises in clusters of needles which deliquesce on exposure to the air, and lose only a part of their water when heated at  $205^\circ$ ; it melts at about  $200^\circ$  and decomposes at  $250$ — $260^\circ$ ; water and spirit dissolve it very readily in the cold, whilst hot absolute alcohol dissolves it but sparingly. The *copper salt*,  $(NH\dot{A}c.CH_2.COO)_2Cu.4\frac{1}{2}H_2O$ , crystallises in azure-blue needles, loses  $3\frac{1}{2}H_2O$  at  $105^\circ$ , and decomposes a little above  $120^\circ$ ; it is very readily soluble in cold water and in hot absolute alcohol. The *thallium salt*,  $NH\dot{A}c.CH_2.COOTl.2(?)H_2O$ , forms small lustrous crystals resembling anatase, easily soluble in cold water. The *nickel, magnesium, lead, and mercurous salts* are also crystalline. The *methyl salt*,  $NH\dot{A}c.CH_2.COOMe$ , forms long colourless rhomboidal plates, melts at  $58.5^\circ$ , and boils at  $254^\circ$  (712 mm.); it is sparingly soluble in boiling ether, very readily in alcohol, chloroform, benzene, and water. The *ethyl-derivative*,  $NH\dot{A}c.CH_2.COOEt$ , crystallises in large rhombic plates, is hygroscopic, and very readily taken up by all solvents; it melts at  $48^\circ$  and boils at  $260^\circ$  (712 mm.). The conversion of ethyl aceturate into ethyl acetylglucollate,  $CH_2(O\dot{A}c).COOEt$ , by the action of chlorine on its alkaline solution (*Annalen*, 99, 181) is very imperfect, the chlorine attacking the acetyl-group, and the ethyl acetylglucollate being much more readily decomposed by alkalis than the corresponding benzoyl-compound. A quantitative method of preparing it consists in boiling ethyl diazoacetate with glacial acetic acid,  $N_2CH_2.COOEt + AcOH = CH_2(O\dot{A}c).COOEt + N_2$ . When ethyl aceturate is gently heated with aqueous ammonia, ammonium acet-

urate is formed together with *aceturamide*,  $\text{NH}\bar{\text{Ac}}\cdot\text{CH}_2\cdot\text{CONH}_2$ . This crystallises in large colourless plates melting at  $137^\circ$ ; it is insoluble in ether, readily soluble in alcohol and water, and, when boiled with these, is rapidly decomposed with evolution of ammonia.

A. K. M.

**Glutamic Acid.** By C. SCHEIBLER (*Ber.*, **17**, 1725—1729). The author has prepared a quantity of this acid from beetroot molasses obtained in working the strontium process. Oebbeke has examined and measured crystals of this acid, and of its hydrochloride, side by side with crystals of Ritthausen's glutamic acid, and declares them to be identical. The author has made determinations of the rotary power of glutamic (amidoglutaric) acid and its salts as likely to prove of value in determining the sugar remaining in molasses. A Soleil-Scheibler polariscope was used with a column of solution 220 mm. long. A 2 per cent. solution of the free acid at  $21^\circ$  had a sp. gr. 1.0070, and a rotation  $1.3^\circ$ , giving  $[\alpha]_j = +11.6^\circ$  or  $[\alpha]_D = +10.2^\circ$ . A 4 per cent. solution, rapidly cooled to prevent crystallisation, gave a rotation  $2.7^\circ$  at  $23^\circ$ , or  $[\alpha]_j = +12.0^\circ$ , or  $[\alpha]_D = +10.6^\circ$ . A solution containing calcium salt equivalent to 2 per cent. had a sp. gr. 1.0240 at  $20^\circ$  and a rotation  $-1.2^\circ$  at  $22^\circ$ . This gives for the salt  $[\alpha]_j = -4.2^\circ$  or  $[\alpha]_D = -3.7^\circ$ ; and for the acid in the salt  $[\alpha]_j = -5.3^\circ$  or  $[\alpha]_D = -4.7^\circ$ . A 4 per cent. solution of the hydrochloride ( $= 3.205$  per cent. acid) had a sp. gr. 1.0158 at  $19^\circ$  and a rotation  $+5.2$ , giving for  $\text{C}_6\text{H}_9\text{NO}_4\cdot\text{HCl}$   $[\alpha]_j = +23.1^\circ$  or  $[\alpha]_D = +20.4^\circ$ , or for the acid therein  $[\alpha]_j = +28.9^\circ$  or  $[\alpha]_D = 25.5^\circ$ . A nitric acid solution shows strong dextro-rotation, varying in amount according to the quantity of nitric acid employed in the solution. L. T. T.

**Uric Acid.** By E. FISCHER (*Ber.*, **17**, 1776—1788).—In continuation of his previous communication (this vol., 996), the author describes several more derivatives of uric acid which he has obtained, and then enters into a theoretical discussion as to the constitution of uric acid.

**Monomethyluric Acids.**—The  $\alpha$ -acid described by Hill (this Journal, 1876, ii, 75) yields monomethylalloxan and carbamide on oxidation: when heated with concentrated hydrochloric acid, it splits up into carbonic anhydride, ammonia, methylamine, and glycocine. The  $\beta$ -acid, briefly described by the author (this vol., 996) under the name of trihydroxymethylpurin, is best prepared by heating dichlorhydroxymethylpurin with concentrated hydrochloric acid at  $135$ — $140^\circ$ . The ammonium salt is not decomposed when the excess of ammonia used in its preparation is boiled off, but on cooling separates from the solution as a gelatinous mass. When treated with an ammoniacal solution of silver nitrate, silver is deposited. When heated with phosphoric chloride and oxychloride at  $130^\circ$ , it is partly reconverted into dichlorhydroxypurin. When oxidised with nitric acid or chlorine-water it is easily decomposed into alloxan and methylcarbamide. When heated for five or six hours at  $170^\circ$  with about five times its weight of strong hydrochloric acid, it is decomposed, yielding the same products as the  $\alpha$ -acid.

**Dimethyluric Acids.**—The  $\alpha$ -acid of Hill is decomposed on oxidation



into monomethylalloxan and monomethylcarbamide: when heated with hydrochloric acid at  $170^{\circ}$ , it yields ammonia, methylamine, and glycocine. Its ammonium salt, unlike that of the  $\alpha$ -mono-acid, is decomposed by boiling—the free acid being re-formed. When heated for some time at  $125^{\circ}$  with phosphoric chloride and oxychloride, an unstable chlorinated compound is produced which, however, differs altogether from the chlorinated body obtained from the  $\beta$ -acid. The  $\beta$ -acid (already described under the name of trihydroxydimethylpurin) is decomposed when heated with hydrochloric acid at  $170^{\circ}$ , yielding carbonic anhydride, ammonia, methylamine, and sarcosine. Its ammonium salt is not decomposed by boiling. When heated with phosphoric chloride and oxychloride at  $135^{\circ}$ , it is almost entirely reconverted into dichloroxydimethylpurin. When oxidised with nitric acid or chlorine-water, traces only of alloxan are produced, the principal product being a body of the composition  $C_7H_{10}N_4O_5$ . It is formed according to the equation  $C_7H_8N_4O_3 + H_2O + O = C_7H_{10}N_4O_5$ , and is a derivative of mesoxalic acid. It has no analogue in the oxidation-products of any of the uric acid derivatives, and the author proposes to name it *oxy- $\beta$ -dimethyluric acid*. It crystallises in large, colourless, and well-formed plates, melts at  $173$ – $174^{\circ}$ , and is completely decomposed at a slightly higher temperature. When its aqueous solution is boiled, decomposition sets in, gas is evolved freely, and easily soluble products are formed. Ammonia produces no red coloration, hydrogen sulphide has no action, but hydriodic acid reduces it, forming an easily soluble crystalline compound still under investigation. Barium hydroxide gives no precipitate with a cold aqueous solution of the compound, but on heating barium mesoxalate is at once precipitated, whilst carbamide, and probably dimethylcarbamide, remain in solution. When oxidised with chromic mixture, it yields cholestrophane,  $C_5H_6N_2O_3$ : this formation of cholestrophane proves that both methyl-groups in this compound, and consequently in  $\beta$ -dimethyluric acid, are combined with the two nitrogen-atoms which are split off from  $\beta$ -monomethyluric acid in the form of monomethylcarbamide. *Consequently it is clear that in uric acid there is a carbamido-group containing two imido-groups distinct from the nucleus which is removed as alloxan on oxidation in acid solution.*

*Trimethyluric Acid.*—The author has not been successful in his attempts to methylate  $\alpha$ -dimethyluric acid. When the lead salt of  $\beta$ -dimethyluric acid, however, is heated for eight hours at  $125$ – $130^{\circ}$  with an equal weight of methyl iodide and double its weight of ether, the product boiled with water, the hot extract treated with sulphuretted hydrogen, and the filtrate supersaturated with ammonia and concentrated to a small bulk, trimethyluric acid separates out as a white crystalline mass melting at  $345^{\circ}$ . It is slightly soluble in alcohol and chloroform, readily in strong hydrochloric acid. It is more easily soluble in ammonia than in water, but the ammonium salt is decomposed again by boiling. Its alkaline salts crystallise in needles. With ammoniacal silver, it yields a crystalline compound containing silver and ammonia; this is easily soluble in hot water, and with excess of silver nitrate yields a pale yellow gelatinous precipitate. If, however, the acid is dissolved in a large quantity of hot ammonia, the calculated



10c.c. HNO <sub>3</sub> + x c.c. H <sub>2</sub> O.	Toluene.		Chloro- benzene.		Bromo- benzene.		Benzylnitranilide.					
	Days.		Days.		Days.		Ortho.	Meta.	Para.	Hours.		
	1.	10.	1.	10.	1.	10.	1.	50.	1.	50.	1.	50.
x = 0 ..	94.6	114	88.5	93.3	107.3	115	210	240	215	224	224	233
1 ..	—	87.4	—	—	—	—	—	—	—	—	—	—
2 ..	—	—	—	—	—	—	97	207	50	201	38	220
2.5 ..	—	—	81.7	87.1	101.3	104.4	—	—	—	—	—	—
4 ..	—	—	—	—	—	—	0	0	0	0	0	34
5 ..	22.5	80.8	4.4	19.7	0	66.6	—	—	—	—	—	—
6 ..	—	—	—	—	—	—	—	—	—	—	—	0
7.5 ..	14.2	32.8	—	—	—	—	—	—	—	—	—	—
20 ..	—	15.8	—	—	—	—	—	—	—	—	—	—

The author's theoretical conclusions on this subject have been already published (*loc. cit.*). W. C. W.

**Replacement of Amido-groups in Aromatic Derivatives by Chlorine.** By T. SANDMEYER (*Ber.*, 17, 1633—1635).—In an attempt to prepare phenylacetylene by the action of cuprous acetylide on diazobenzene chloride, *chlorobenzene* was obtained. This result is due to the formation of cuprous chloride, and is best carried out as follows: 150 grams of a 10 per cent. solution of cuprous chloride in hydrochloric acid are heated almost to boiling in a flask provided with a reflux condenser, and a solution of diazobenzene chloride is then gradually added, the whole being kept well shaken; each drop of the diazobenzene solution produces a yellow precipitate which, however, at once decomposes with evolution of nitrogen. The product is distilled in a current of steam, dried and fractioned, when chlorobenzene is obtained of constant boiling point (130°). In explanation of this reaction, the author suggests the two equations:  $\text{PhN}:\text{NCl} + \text{Cu}_2\text{Cl}_2 = \text{PhN}(\text{CuCl})\cdot\text{N}(\text{CuCl})\text{Cl}$  and  $\text{PhN}(\text{CuCl})\cdot\text{N}(\text{CuCl})\text{Cl} = \text{N}_2 + \text{Cu}_2\text{Cl}_2 + \text{PhCl}$ , the intermediate compound  $\text{PhN}(\text{CuCl})\cdot\text{N}(\text{CuCl})\text{Cl}$  being, perhaps, the yellow precipitate mentioned. Cupric and ferrous chlorides do not act in this way. Metamidobenzoic acid has in the same way been converted into metachlorobenzoic acid, and the reaction simplified by treating a mixture of the amido-compound and cuprous chloride with potassium nitrite. The author is trying the reaction with other substances, and already finds that it holds with metanitriline and paraphenylenediamine. A. K. M.

**Reaction of Iodine with Carbon Compounds at High Temperatures.** By B. RAÝMAN and K. PREIS (*Annalen*, 223, 315—323).—In earlier communications (*Abstr.*, 1879, 623; 1880, 463), the authors have shown that by the action of iodine at 250° on aromatic compounds containing long side-chains, the side-chains are separated and split into methyl-groups which then enter the aromatic nucleus, forming methyl, dimethyl, &c., derivatives, the most probable course of the reaction being that methyl iodide substitution-derivatives of the aromatic nucleus are first formed, and by their further action

yield free iodine and aromatic methyl substitution-derivatives. In accordance with this view, the present experiments were made by heating at 250° aromatic hydrocarbons with alkyl iodides and a small quantity of iodine. To remove the hydriodic acid formed in some cases the corresponding alkyl bromide, in others isobutyl alcohol was added.

Benzene with methyl iodide and iodine yielded methane, toluene, and higher hydrocarbons not investigated.

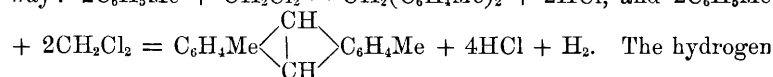
Toluene with ethyl iodide and iodine gave xylenes (principally metaxylene), a hydrocarbon,  $C_9H_{12}$  (ethyltoluene?) and hydrocarbons of higher boiling point, probably hydrides and ethylphenyls.

Metaxylene with iodine and methyl iodide yielded pseudocumene, mesitylene, a hydrocarbon,  $C_{10}H_{14}$ , most probably identical with that prepared by Holtmeyer (*Zeit. f. Chem.*, 1867, 689) from mesitylene, and a hydrocarbon,  $C_{11}H_{16}$ , distilling between 205° and 223°.

Commercially pure pseudocumene (pseudocumene and mesitylene) with ethyl iodide and iodine gave symmetrical (?) ethyldimethylbenzene.

Hexyl iodide, when heated with iodine for five hours at 256°, yields a combustible gas and hydriodic acid in large quantities, methyl iodide in small quantity, the main product being hexane. A. J. G.

**Action of Methylene Chloride on Toluene and Benzene.** By C. FRIEDEL and J. M. CRAFTS (*Bull. Soc. Chim.*, 41, 322—327).—Ditolylmethane, dimethylantracene, together with para-, meta-, and probably ortho-xylene, are obtained by acting on toluene boiling at 110—111°, with methylene chloride boiling at 40—45°, in presence of aluminium chloride. The reactions are represented in the following way:  $2C_6H_5Me + CH_2Cl_2 = CH_2(C_6H_4Me)_2 + 2HCl$ , and  $2C_6H_5Me$



liberated in this reaction reduces the methylene chloride to methyl chloride, and this reacting with toluene in presence of aluminium chloride yields xylene; para- and meta-xylene were recognised by their oxidation-products, but the ortho variety was also probably produced. When benzene is treated with methylene chloride in presence of aluminium chloride, diphenylmethane and anthracene are obtained, and also, by a secondary reaction, toluene. The decompositions are  $C_6H_6 + CH_2Cl_2 = CH_2(Ph)_2 + 2HCl$ ;  $2C_6H_6 + 4CH_2Cl_2 = C_{14}H_{10} + 4HCl + 2MeCl$ ; and  $C_6H_6 + MeCl = C_6H_5Me + HCl$ . The results obtained by Schwarz are attributable to the use of methylene chloride containing chloroform. W. R. D.

**Action of Isobutyl Chloride on Benzene.** By E. GOSSIN (*Bull. Soc. Chim.*, 41, 446—447).—By the action in the cold of 50 grams of isobutyl chloride (boiling at 68—69°) on 150 grams of benzene and about 50 grams of aluminium chloride, two liquids of the formula  $C_{10}H_{14}$  are obtained. The one boils at 166—167°, and is identical with the compound obtained by Fittig from bromobenzene and isobutyl bromide; the other boils at 152—155°, and is formed only in very small quantity, it appears to be tertiary butylbenzene.

W. R. D.

**Derivatives of Metaxylene.** By A. COLSON (*Compt. rend.*, **99**, 40—42.)—Crude xylene is not entirely freed from paraxylene even by two successive treatments with dilute nitric acid, and the dibromo-derivative described by Radziszewski and Wispek as dibromometaxylene (melting at 140—141°), is really dibromo-*para*-xylene in a more or less pure condition.

*Dibromometaxylene*,  $C_6H_4(CH_2Br)_2$ , is obtained from the pure metaxylene of commerce by the same method as the ortho-derivative, and may be purified by recrystallisation from light petroleum, or, if ebullition and too long contact are avoided, from alcohol of 90°. It forms white crystals which melt at 77·1°, and dissolve in ether and chloroform, in three times their weight of boiling light petroleum, and in a smaller quantity of boiling alcohol. Sp. gr. of the crystals at 0° = 1·734; of the liquid at 90° = 1·61.

*Metaxylene glycol*,  $C_6H_4(CH_2.OH)_2$ , is obtained by saponifying the dibromo-derivative with an aqueous solution of potassium carbonate, evaporating to dryness on the water-bath, and extracting with ether. On slow evaporation, the ether leaves an oily liquid which quickly solidifies in microscopic crystals melting at 45·5—46·2°. The crystals are inodorous and have a bitter taste. They dissolve in about seven times their weight of ether at 12°, but are much more soluble in water and very readily form supersaturated solutions. They also have a tendency to remain in superfusion; the sp. gr. of the liquid at 18° is 1·16. On oxidation, metaxylene glycol yields isophthalic acid, and when treated with concentrated aqueous hydrobromic or hydrochloric acid, yields the corresponding bromide or chloride. Dichlorometaxylene is a crystalline compound which melts at 34·2°.

The following table gives the melting point of several derivatives of the xylenes:—

	Para.	Ortho.	Meta.
Dichloroxylylene ...	100·5°	54·5°	34·2°
Dibromoxylylene ...	143·0	94·9	77·1
Xyleneglycol .....	112·5	64·6	46·2
Xylene .....	16·0	?	?

C. H. B.

**Orthoxylylene-derivatives.** By G. LESER (*Ber.*, **17**, 1824—1826).

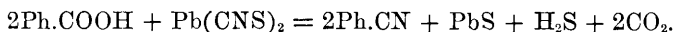
—*Orthoxylylene sulphide*,  $C_6H_4<\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}>S$ , was prepared by treating an alcoholic solution of orthoxylylene bromide with a saturated aqueous solution of potassium sulphide, and then distilling in a current of steam. It is a colourless oil, with a strong odour of mercaptan. It distils undecomposed, and solidifies to large crystals a little above 0°. *Orthoxylylenediethyl ether*,  $C_6H_4(CH_2.OEt)_2$ , is obtained by boiling orthoxylylene bromide with a large excess of alcoholic potash. It is a light colourless oil of pleasant odour, and boils at 247—249° under 720 mm. pressure. *Orthoxylylenediunilide* (or diphenylorthoxylylenediamine),  $C_6H_4(CH.NHPh)_2$ , is obtained by boiling an alcoholic solution of orthoxylylene bromide with an excess of aniline. It crystallises from alcohol in small colourless needles melting at 172°. It is a feeble base, and is soluble in concentrated hydrochloric acid,

but is reprecipitated from this solution on the addition of water. *Orthoxylylene iodide* is obtained by digesting the bromide with excess of potassium iodide, or better by treatment of phthalic alcohol (xylylene hydroxide) with fuming hydriodic acid and amorphous phosphorus. It crystallises from ether in well-formed yellow prisms, melting at 109—110°. L. T. T.

**Preparation of Nitriles.** By G. KRÜSS (*Ber.*, **17**, 1766—1768).—Letts showed (this Journal, **25**, 1020) that most of the aromatic nitriles may be prepared by heating potassium thiocyanate with the respective aromatic acids, the reaction taking place according to the equation—



By this reaction only half the acid employed is converted into the nitrile. By substituting lead thiocyanate in place of the potassium salt, the author is enabled to convert the whole of the acid into its nitrile,



The acid and thiocyanate are heated together in the dry state at 190—195°. In preparing benzonitrile by this process, the author obtained 50—60 grams nitrile from 100 grams benzoic acid, as compared with 33 grams obtained by Letts. Letts was unable to obtain cinnamonitrile by his method, the decomposing point of potassium thiocyanate lying below the temperature necessary for the reaction. Lead thiocyanate being more active than the potassium salt, the author succeeded in preparing cinnamonitrile by the new process, obtaining 5 grams nitrile from 15 grams acid. L. T. T.

**Nitration of Thiophene-derivatives.** By H. KREIS (*Ber.*, **17**, 2073—2075).—Although thiophene and its homologues are completely oxidised by treatment with nitric acid, thiophene-derivatives containing negative groups can be nitrated.

*Iodonitrothiophene*,  $C_4SH_2I.NO_2$ .—On mixing iodothiophene with excess of nitric acid at the ordinary temperature, a violent reaction takes place, and the compound is completely oxidised. If the nitric acid is added drop by drop, however, with continued shaking, and cooling between each addition of acid, the required nitro-compound is formed. It crystallises in lemon-yellow prisms, has an intense bitter-almond-like odour, melts at 74°, and is soluble in alcohol; insoluble in water.

*Dibromodinitrothiophene*,  $C_4SBr_2(NO_2)_2$ , is prepared by suspending dibromothiophene in five times its volume of sulphuric acid, and adding nitric acid drop by drop. It is unnecessary to cool the mixture. It forms hard, pale-yellow crystals, which melt at 134°; it is readily soluble in hot, but only sparingly in cold alcohol.

A. J. G.

**Conversion of Aromatic Amines into the Ethers of the corresponding Phenols.** By A. W. HOFMANN (*Ber.*, **17**, 1917—1920).—In order to obtain tetramethylbenzene (see p. 1320) more easily than by the action of hydrochloric acid on the nitrile, the

author converted tetramethylamidobenzene into the diazo-compound, and boiled that with alcohol. Instead of the expected hydrocarbon, he obtained the *ethyl ether*,  $C_6HMe_4.OEt$ , an aromatic oil boiling at  $236-237^\circ$ .

In order to determine whether this was a special reaction of the body in question, or of more general application, he has prepared several more diazo-compounds, and decomposed them by means of alcohol.

Cumidine thus treated yielded the ether  $C_6H_2Me_3.OEt$ , boiling at  $223-224^\circ$ , together with a sparingly soluble crystalline substance which melts at  $173^\circ$ , and is now undergoing investigation. When methyl and amyl alcohols were substituted for ethyl alcohol, the methyl and amyl ethers were obtained respectively. The *methyl ether* boils at  $213-214^\circ$ , the *amyl ether* at  $265-266^\circ$ .

The reaction was also tried with aniline, toluidine, &c., and in all cases the corresponding ethers were formed, sometimes together with a small quantity of the hydrocarbon. It is therefore clear that when a diazo-compound is boiled with alcohol the diazo-group displaced is not always replaced by hydrogen, but often by an oxy-radicle (ethoxyl, methoxyl, &c.) (see also Haller, this vol., p. 1322). L. T. T.

**Action of Nitro-hydrobromic Acid on Organic Compounds.** By H. BRUNNER and C. KRAEMER (*Ber.*, **17**, 1872-1874).—The authors are now engaged in investigating the action of a mixture of hydrobromic and nitric acids on inorganic and organic substances, to determine whether it acts in a manner analogous to aqua-regia. The present communication treats of some compounds of interest in relation to the authors' work on the phenol-colouring matters (see this vol., pp. 1333 and 1340).

Aniline, dimethylaniline, diphenylamine, phenol, quinol, catechol, and  $\alpha$ -naphthol yield no colouring matters when treated with nitro-hydrobromic acid. Resorcinol yields a lustrous green mass which dissolves in alcohol to a red solution; this, on the addition of an alkali, turns blue, and shows a brown fluorescence. This colouring matter has the formula  $C_{35}H_{25}BrN_2O_{10}$ ; it probably must be considered as a brominated derivative of the compound  $C_{35}H_{26}N_2O_{10}$ .

With nitro-hydrobromic acid, orcinol yields a reddish-brown amorphous body containing bromine; this is being investigated.

L. T. T.

**Condensation-products of Aromatic Bases with Aldehydes.** By O. FISCHER and C. SCHMIDT (*Ber.*, **17**, 1889-1896).—I. *Orthonitrobenzaldehyde and Dimethylaniline*.—The leuco-base orthonitrotetramethyldiamidotriphenylmethane thus produced has been already described (*Abstr.*, 1882, 834). Its crystals are monoclinic, and measurements thereof gave  $a:b:c = 1.1795:1.05262$  and  $\beta = 85^\circ 0'$ . Its melting point is  $159-160^\circ$ . By oxidation of the sulphate of this leuco-base with lead dioxide, the colour-base *orthonitro-malachite-green*,  $C_{23}H_{25}N_3O_3$ , is obtained. It forms small, orange, lustrous crystals which melt at  $163^\circ$ . It is easily soluble in benzene, ether, and alcohol. Its neutral salts are green, with a blue shade. The reduction-product already described (*loc. cit.*) forms with benzene

colourless crystals melting at 134—135°. The leuco-base, when boiled with acetic anhydride, yields a monacetyl-derivative, melting at 186°. This body, when oxidised with a peroxide, yields *acetamidobenzaldehyde green*, a beautiful green colouring matter. When the acetyl-compound is converted into its sulphate before oxidation, the acetyl is eliminated during the reaction,  $C_{23}H_{27}N_3O$  being formed. The neutral salts of this base are green, with a blue shade. The introduction of a nitro- or amido-group into the benzene nucleus, in the para-position to the methane-group, thus causes a tendency of the colour towards blue, whilst, as is known, these groups in the meta-position scarcely alter the colour-shade.

II. *Orthonitrobenzaldehyde and Diethylaniline*.—Analogous compounds are produced with diethylaniline. *Orthonitrotetrazyldiamidotriphenylmethane* melts at 109—110°. Its crystals are of a reddish-orange, belong to the triclinic system, and give  $a:b:c = 0.7720:1:0.8037$ , and  $\alpha = 100^\circ 55'$ ,  $\beta = 95^\circ 52'$ ,  $\gamma = 94^\circ 38'$ . The *amido-base* crystallises in needles melting at 136°. The *colour-base* is a deep bluish-green.

III. *Vanilline and Dimethylaniline*.—The *leuco-base*,  $C_{24}H_{28}N_2O_2$ , melts at 135—136°, and forms colourless crystals. The *colour-base* is violet.  
L. T. T.

**Nitrotoluidine (m. p. 91.5°) prepared from Liquid Dinitrotoluene.** By C. ULLMANN (*Ber.*, 17, 1957—1964).—Bernthsen has shown (*Abstr.*, 1883, 579) that two nitrotoluidines are obtained on reducing liquid dinitrotoluene, the one  $[Me:NO_2:NH_2 = 1:2:4]$  already known, and a second melting at 91.5°, and yielding a benzoyl-derivative melting at 167—167.5°. This latter had been previously obtained in an impure form by Cunerth (*this Journal*, 1875, 82), who had shown the methyl- and nitro-groups to be relatively in the ortho-position. The author confirms this result, and further shows that by conversion of the nitrotoluidine into a nitrocresol, of this into the amidocresol, and by then eliminating the amido-group by Griess's reaction, orthocresol is obtained. The nitrotoluidine, therefore, must have the constitution  $[Me:NO_2:NH_2 = 1:2:6]$ .

1:2:6 *Nitrotoluidine* crystallises in long silky needles, and is readily soluble in alcohol, ether, and benzene. The *hydrochloride*,  $C_6H_3Me(NO_2).NH_2.HCl$ , crystallises in long flat needles, readily soluble in water, and also readily decomposed by it. When heated, it begins to lose hydrochloric acid at 80°. The *sulphate* forms small crystals, relatively sparingly soluble in water. The *acetyl-compound*,  $C_6H_3Me(NO_2).NHAc$ , obtained by the action of acetic chloride on an alcoholic solution of the base, crystallises in long, brilliant, colourless needles, melts at 157.5—158°, is readily soluble in alcohol and ether, sparingly soluble in cold water.

*Toluylenediamine*,  $C_6H_3Me(NH_2)_2[1:2:6]$ .—The hydrochloride is obtained by heating nitrotoluidine on the water-bath with tin, hydrochloric acid, and stannous chloride; it crystallises in thick colourless needles. The free base, prepared by the dry distillation of the hydrochloride with lime, crystallises in yellowish-white prisms, and melts



at 103.5°. It appears to be more stable than its isomerides. The aqueous solution turns brown slowly on exposure to air. Its solution in sulphuric acid gives a yellowish-brown coloration with potassium nitrite. With paranitrosodimethylaniline it gives, first a green, and then a blue coloration, turning violet on long standing; ordinary 1 : 2 : 4 toluylenediamine gives the same reaction. With ferric chloride, or with chromic acid, it gives a deep brown coloration.

*Nitrocresol*,  $C_6H_3Me(NO_2).OH$  [1 : 2 : 6], prepared by means of the diazo-reaction from the 1 : 2 : 6 nitrotoluidine, crystallises in woolly yellow needles, melts at 142—143°, is very sparingly soluble in cold water, readily soluble in alcohol and ether, soluble in aqueous baryta or soda, with intense yellowish-red. colour. The alkali compounds could not be isolated. Silver nitrate gives a white precipitate, sparingly soluble in ammonia, and crystallising from dilute nitric acid in interlaced needles.

*Amidocresol*,  $C_6H_3Me(NH_2).OH$  [1 : 2 : 6], is obtained as hydrochloride by the reduction of the nitrocresol with tin and hydrochloric acid; by treating this with sodium carbonate, the free base may be obtained, crystallising in concentrically grouped needles. It melts at 124—128°; is sparingly soluble in cold water and ether. It dissolves in soda and ammonia, without characteristic coloration. By heating it with sulphuric acid, and then pouring into water, a solution is obtained green by reflected, flesh-coloured by transmitted light. The *hydrochloride* crystallises in white needles, can be sublimed, is readily soluble in water and alcohol. It is stable in the pure and dry condition, but very unstable if impure.

*Dihydroxytoluene*,  $C_6H_3Me(OH)_2$  [1 : 2 : 6], was prepared from the 1 : 2 : 6 amidocresol by Neville and Winther's method (Trans., 1882, 415). The yield was very small. It crystallises in nearly colourless needles, melts at 63—66°, has a biting taste and phenol-like odour, and is readily soluble in water or alcohol. It dissolves readily and without coloration in soda and in ammonia, the solution in the latter slowly turning a pale dirty blue. It gives a white precipitate with bromine-water, a magenta coloration rapidly changing to yellowish-brown with bleaching-powder, a rose-red with chloroform and soda. It reduces ammoniacal silver solution in the cold. By heating it with phthalic anhydride, and dissolving the product in soda, a rose-red liquid, with strong green fluorescence, is obtained. It is probably identical with  $\gamma$ -isoreinol, but it is impossible, from the small yield, to speak as yet with certainty. A. J. G.

**Action of Dimethylparatoluidine and Dimethylaniline on Ethylene Bromide.** By H. HÜBNER, A. TÖLLE, and W. ATHENSTÄDT (*Annalen*, 224, 331—353).—*Ethylene ditolyldimethylammonium bromide*,  $(C_7H_7Me_2NBr)_2C_2H_4$ , and a small quantity of ethylene ditolylmethylamine,  $(C_7H_7MeN)_2C_2H_4$ , are formed when a mixture of ethylene bromide and dimethylparatoluidine is heated at 100—110° in sealed tubes for four days. The product is dissolved in water and boiled, in order to remove unaltered dimethyltoluidine and ethylene bromide. On cooling, a portion of the amine crystallises out, and the remainder is precipitated by ammonia. The solution of ethylene di-

tolyldimethylammonium bromide is converted into the carbonate by the action of silver carbonate. The single salts of this base are very soluble in alcohol and water; the double salts crystallise readily. The platinochloride,  $(C_7H_7Me_2NCl)_2C_2H_4, PtCl_4$ , forms orange-coloured needles; the mercuriochloride,  $(C_7H_7Me_2NCl)_2C_2H_4, 2HgCl_2$ , and stannichloride,  $(C_7H_7Me_2NCl)_2C_2H_4, SnCl_4$ , crystallise in colourless needles. The picrate forms pale-yellow needles or plates which melt at  $196^\circ$ . The aqueous solution of the carbonate is decomposed by heat, yielding ethylenedimethyltolylamine. This amine crystallises in colourless plates or prisms melting at  $80^\circ$ ; and dissolves freely in benzene or ether. The hydriodide forms rhombic plates, the oxalate colourless needles, the platinochloride,  $(C_7H_7MeN)_2C_2H_4, H_2PtCl_6$ , an orange powder, and the mercuriochloride thick needles. Almost all the salts are unstable, and are very soluble in water. Two mols. of ethylenedimethyltolylamine unite with 1 mol. of methyl iodide, forming *ethylenemethyltolylamine-dimethyltolylammonium iodide*,  $C_7H_7Me.NC_2H_4.NI(C_7H_7Me_2)$ , a colourless crystalline compound, soluble in hot water. The corresponding carbonate is insoluble in water. The double salt with mercuric chloride is crystalline. Ethylenedimethyltolylamine is decomposed by heat, yielding triethylenetritolylamine,  $(C_6H_4Me.N : C_2H_4)_3$ , and dimethyltolylamine. Ethylene bromide acts on dimethylaniline at  $100^\circ$ , forming *ethylenediphenyldimethylammonium bromide*,  $(PhMe_2NBr)_2C_2H_4$ , a deliquescent salt, deposited from an alcoholic solution in colourless prisms. The corresponding hydroxide dissolves in water, yielding a solution which absorbs carbonic anhydride, forming a crystalline carbonate. The aqueous solution of the carbonate is not decomposed by boiling, but the carbonate is decomposed by dry distillation, forming dimethylaniline.

The *chloride*,  $(PhMe_2NCl)_2C_2H_4$ , crystallises in deliquescent prisms, freely soluble in alcohol, and the picrate forms yellow needles melting at  $124^\circ$ ; it dissolves sparingly in cold alcohol or water.

The following table shows the chief points of difference between the salts of trimethylphenylammonium and those of ethylenediphenyldimethylammonium:—

	Trimethylphenyl- ammonium.	Ethylenediphenyldi- methylammonium.
Mercuriochloride ...	Deposited from water in colourless needles.	The same.
Solubility in $H_2O$ ..	M. p. $187^\circ$ . 1 in 275.5 at 6.2	M. p. $175^\circ$ . 1 in 317.9 at 6.2.
Platinochloride ....	Deposited from water in yellowish-red needles.	The same.
Soluble in $H_2O$ ....	1 in 304.9 at 7.4	1 in 404.8 at 7.4.
Iodide .....	Deposited from alcohol in colourless plates.	The same.
Soluble in alcohol ..	1 in 45.5 at 8.2	1 in 46.4 at 8.2.
Dichromate.....	1 in 200 of cold water.	1 in less than 75 parts of cold water.

W. C. W.

**Derivatives of Pseudocumidine.** By E. FRÖHLICH (*Ber.*, 17, 1801—1809).—*Phthalopseudocumide*,  $C_6H_2Me_3N : C_8H_4O_2$ , was prepared by heating cumidine with phthalic anhydride. It crystallises in rhombic prisms, melts at  $148^\circ$ , and distils without decomposition at a temperature above the boiling point of mercury. It is easily soluble

in carbon bisulphide, chloroform, and benzene, sparingly so in alcohol and ether, and insoluble in water. It sometimes crystallises in needles which, however, change back to the prisms on shaking, or often spontaneously.

*Benzoylphthalopseudocumide*,  $C_6HBzMe_3N : C_8H_4O_2$  is formed when a mixture of phthalopseudocumide and benzoic chloride is heated with a little zinc chloride at  $175-180^\circ$  for 8 hours. It crystallises in small glittering rhombohedra which melt at  $181^\circ$ , and are readily soluble in boiling acetic acid, sparingly so in alcohol, ether, and carbon bisulphide, insoluble in water. When quickly distilled in small quantities, it passes over unchanged, but is totally decomposed if distilled in large quantity or slowly.

*Benzoylpseudocumidine*,  $C_6HBzMe_3.NH_2$ , is prepared by the saponification of the compound just described, with concentrated sulphuric or hydrochloric acid at  $140-150^\circ$ . If saponified with alcoholic potash an intermediate compound,  $C_6HBzMe_3.NH.CO.C_6H_4.COOH$ , is first formed; and heating in closed tubes at  $100^\circ$  for 24 hours must be resorted to to complete the saponification. Benzoylpseudocumidine crystallises in lemon-yellow needles or scales which melt at  $130^\circ$ . It is easily soluble in alcohol, ether, benzene, and chloroform, almost insoluble in water, and is not volatile with steam. It forms crystallisable salts with one equivalent of acid. The platinochloride  $(C_{16}H_{17}NO)_2.H_2PtCl_6$ , crystallises in orange needles. With benzoic chloride it yields benzoylbenzopseudocumide,  $C_6HBzMe_3.NHBz$ , which forms colourless glittering needles; it melts at  $227^\circ$ , and is sparingly soluble in ether and alcohol, easily in boiling glacial acetic acid, insoluble in water.

*Benzoylpseudocuminal*,  $C_6HBzMe_3.OH$ , is obtained from the cumidine by means of the diazo-reaction. It yields colourless micaceous scales melting at  $187^\circ$ . It is easily soluble in alcohol and ether, insoluble in water, but dissolves in sodium hydroxide. It is not volatile with steam.

*Phthalopseudocumidamide*,  $C_6H_4(CONH_2).CONH.C_6H_2Me_3$ , is obtained when a hot saturated solution of phthalopseudocumide is treated with a slight excess of ammonia. It crystallises in colourless needles, melts at  $218^\circ$ , and is decomposed at that temperature into ammonia and phthalocumide. It is sparingly soluble in alcohol. It is of interest as being the first phthalamide which has been obtained, all attempts to prepare such an amide having previously led to the formation of the corresponding imide. Sulphuric acid decomposes this body into phthalic acid and cumidine without the formation of a trace of sulphonic acid. If methylamine be substituted for ammonia in the above reaction, *methylphthalopseudocumidamide*,  $C_6H_2Me_3.NH.CO.C_6H_4.CONHMe$ , is formed. This crystallises in needles melting at  $215^\circ$  with decomposition. It is sparingly soluble in alcohol and ether, insoluble in water. *Allylphthalopseudocumidamide*, prepared in like manner, forms silky needles melting at  $179^\circ$  with decomposition. It is easily soluble in alcohol. Di- and tri-methylamine and their homologues, as also aromatic amines, are without action on phthalopseudocumide.

*Phthalopseudocumide acid*,  $C_6H_2Me_3.NH.CO.C_6H_4.COOH$ , is obtained

by heating phthalopseudocumide with alcoholic potash on the water bath for half an hour. It crystallises in colourless needles and melts at  $179^{\circ}$  with decomposition. It is easily soluble in alcohol, chloroform, and glacial acetic acid, sparingly so in ether and carbon bisulphide, insoluble in water. It forms metallic salts, of which the *lead, silver, mercury, and copper* salts are sparingly soluble. The ammonia salt when heated on the water-bath gives up ammonia and water, and reforms phthalopseudocumide. By continued treatment with alcoholic potash or with sulphuric acid it is decomposed into phthalic acid and pseudocumidine.

L. T. T.

**Tetramethylated Amidobenzene.** By A. W. HOFMANN (*Ber.*, 1912—1916).—The author has examined an oil which was formed as a bye-product in the preparation of solid cumidine on a large scale. The crude product boiled between  $240$ — $300^{\circ}$ . As the cumidine was prepared by the action of methyl alcohol on xylydine hydrochloride, it seemed probable that this bye-product would contain methylated homologues of cumidine.

Amongst several substances to be described at a future time, the author succeeded in isolating a pale-yellow oil boiling at  $252$ — $253^{\circ}$ , which proved to be tetramethylamidobenzene,  $C_6HMe_4.NH_2$ . It solidifies at  $11^{\circ}$  to a crystalline mass which melts at  $14^{\circ}$ ; and at  $24^{\circ}$  has sp. gr. 0.978. It is a primary amine, and yields a crystalline hydrochloride and platinochloride. Its salts crystallise well, and are mostly soluble in boiling water. The *dimethylated base*,  $C_6HMe_4.NMe_2$ , was obtained by treating the free base with methyl iodide. It is a colourless liquid, and boils at  $236$ — $235^{\circ}$ . Its platinochloride is crystalline. The *isonitrile*,  $C_{10}H_{13}.NC$ , of the original base, is easily obtained by heating the latter with chloroform and potassium hydroxide. It is a white crystalline substance melting at  $51^{\circ}$ . It has the odour characteristic of isonitriles, but in a very subdued degree. When heated to  $240^{\circ}$  violent reaction sets in, the temperature of the whole rises, and at  $260^{\circ}$  the normal nitrile distils over. This body solidifies on cooling and then melts at  $68$ — $69^{\circ}$ . This nitrile is exceedingly stable, and the author has not yet succeeded in converting it into the corresponding acid. Heated to  $250^{\circ}$  with hydrochloric acid, it is decomposed into a *tetramethylbenzene*,  $C_6H_2Me_4$ , and carbonic anhydride. The author is unable to say yet whether this hydrocarbon is identical or not with that described by Jannasch (*Ber.*, 8, 356). If the original base is digested with carbon bisulphide, sulphuretted hydrogen is evolved, and a thiocarbimide and a thio-carbamide are formed. The thiocarbimide,  $C_6HMe_4.NCS$ , crystallises at  $65^{\circ}$ . When distilled with powdered potash, it yields the base in a very pure state. The *thiocarbamide*,  $CS(NH.C_6HMe_4)_2$ , crystallises in plates which melt at  $278^{\circ}$ . By means of the diazo-reaction, the base was converted into the *phenol*  $C_6HMe_4.OH$ : this forms white crystals melting at  $80$ — $81^{\circ}$ , and has the usual properties of phenols.

L. T. T.

**Secondary Amines.** By W. GEBHARDT (*Ber.*, 17, 2088—2095). This paper deals with the products of the action of isothiocyanates, of isocyanates, of thiocyanates, and of cyanates on secondary amines.

*Methyldiphenylthiocarbamide*,  $NHPh.CS.NMePh$ , prepared by the

action of methylaniline on phenyl isothiocyanate, crystallises in thick rhombic prisms, is readily soluble in benzene, ether, glacial acetic acid, chloroform, and hot alcohol, sparingly soluble in cold alcohol and light petroleum, insoluble in water. It melts at  $87^{\circ}$ , distils at  $204\text{--}206^{\circ}$ . It is resolved into its components by distilling it with steam (when they recombine in the distillate), or by heating it with phosphoric acid. Boiled with aniline it yields thiocarbanilide. In sealed tubes at  $250^{\circ}$ , the reaction between methylaniline and phenyl isothiocyanate takes a different course, dimethylaniline and thiocarbanilide being formed.

*Ethylidiphenylthiocarbamide*,  $\text{NHPh.CS.NEtPh}$ , prepared in like manner from ethylaniline, closely resembles the methyl compound, and melts at  $89^{\circ}$ .

*Phenylmethylparatolylthiocarbamide*,  $\text{NH}(\text{C}_7\text{H}_7).\text{CS.NMePh}$ , prepared from paratolyl isothiocyanate and methylaniline, crystallises in small rhombic tables, melts at  $124^{\circ}$ , is readily soluble in benzene, sparingly in light petroleum.

*Phenylethylparatolylthiocarbamide*,  $\text{NH}(\text{C}_7\text{H}_7).\text{CS.NEtPh}$ , resembles the preceding compound, and melts at  $90^{\circ}$ .

*Phenylmethyl- $\beta$ -naphthylthiocarbamide*,  $\text{NH}(\text{C}_{10}\text{H}_7).\text{CS.NMePh}$ , prepared from methylaniline and  $\beta$ -naphthyl isothiocyanate, forms long yellow needles and melts at  $127^{\circ}$ .

*Triphenylthiocarbamide*,  $\text{NHPh.CS.NPh}_2$ :—Diphenylamine, and phenyl isothiocyanate do not react at ordinary temperatures, but on heating the mixture at  $280^{\circ}$  for several days triphenylthiocarbamide is formed. It crystallises in long white needles, melts at  $152^{\circ}$ , is soluble in hot alcohol and alkalis, sparingly in cold alcohol.

*Methylidiphenylcarbamide*,  $\text{NHPh.CO.NMePh}$ , prepared by mixing methylaniline and phenyl isocyanate, crystallises in small needles, melts at  $104^{\circ}$ , distils at  $203\text{--}205^{\circ}$ , is readily soluble in benzene, ether, chloroform, glacial acetic acid, and hot alcohol, but only sparingly in cold alcohol or hot water, and is almost insoluble in light petroleum and alkalis.

*Ethylidiphenylcarbamide*,  $\text{NHPh.CO.NEtPh}$ , forms large transparent prisms and melts at  $91^{\circ}$ .

*Unsymmetrical methylphenylthiocarbamide*,  $\text{NH}_2.\text{CS.NMePh}$ , is prepared by evaporating to dryness mixed aqueous solutions of methylaniline hydrochloride and excess of potassium thiocyanate. It crystallises in thick, colourless rhombic tables, melts at  $107^{\circ}$ , and is soluble in alcohol, benzene, and hot water.

*Unsymmetrical ethylphenylthiocarbamide*,  $\text{NH}_2.\text{CS.NEtPh}$ , crystallises in long, hard, nacreous prisms and melts at  $113^{\circ}$ .

*Unsymmetrical methylphenylcarbamide*,  $\text{NH}_2.\text{CO.NMePh}$ , prepared from methylaniline hydrochloride and potassium cyanate, crystallises in very thin striated rhombs of fatty lustre, melts at  $82^{\circ}$ , and is readily soluble in all the ordinary solvents with the exception of light petroleum.

*Unsymmetrical ethylphenylcarbamide*,  $\text{NH}_2.\text{CO.NEtPh}$ , forms silvery plates and melts at  $62^{\circ}$ .

The unsymmetrical diphenylcarbamide is not obtained by the action of diphenylamine hydrochloride on potassium cyanate.

A. J. G.

**Action of Ferric Chloride on Orthophenylenediamine.** By F. WIESINGER (*Annalen*, **224**, 353—356).—On the addition of ferric chloride to a solution of orthophenylenediamine hydrochloride, red needle-shaped crystals are deposited, of the composition



The formation of this salt by the action of ferric chloride on orthodiamidobenzene hydrochloride was observed by Griess (*J. pr. Chem.*, **3**, 143; **5**, 202), but its properties were not investigated. The hydrochloride crystallises from water in ruby-coloured plates, containing 5 mols.  $\text{H}_2\text{O}$ . On decomposition with soda, it yields the free base  $\text{C}_{24}\text{H}_{18}\text{N}_6\text{O}$  as a yellow crystalline precipitate, which dissolves sparingly in alcohol and water, with partial decomposition. The *sulphate*,  $\text{C}_{24}\text{H}_{18}\text{N}_6\text{O}, \text{H}_2\text{SO}_4 + 3\text{H}_2\text{O}$ , crystallises in needles, which resemble chromic anhydride in appearance. The *nitrate* is very unstable.

W. C. W.

**New Aniline Colours.** By PETRIEFF (*Bull. Soc. Chim.*, **41**, 310).—Aniline hydrochloride, when treated with an aqueous solution of potassium nitrite, yields a crystalline compound having the formula  $\text{C}_{18}\text{H}_{18}\text{N}_4$ , which melts at  $95^\circ$ , and is soluble in most liquids. Its salts are decomposed by water. It dyes a golden-yellow. When the compound is fused with aniline hydrochloride, a blue dye of the formula  $\text{C}_{30}\text{H}_{26}\text{N}_4$  is obtained, together with a violet product, which probably has the formula  $\text{C}_{24}\text{H}_{22}\text{N}_4$ . The same compound, when fused with  $\alpha$ -naphthol, gives an orange-coloured substance, of the formula  $\text{C}_8\text{H}_{27}\text{N}_4$ , and with  $\beta$ -naphthol an orange-red colouring matter.

W. R. D.

**Action of Alcohol on Diazo-compounds.** By S. HALLER (*Ber.*, **17**, 1887—1889).—It is generally stated that when a diazo-salt is boiled with absolute alcohol, the diazo-group is replaced by hydrogen. But in this reaction there are always many bye-products formed. Diazocumene sulphate, when boiled with alcohol, yields only a very small quantity of hydrocarbon, the principal product being its ethyl ether. Diazobenzene sulphate,  $\beta$ -diazonaphthalene, &c., give similar results. It would seem, therefore, that with the decomposition of diazo-compounds by alcohol, the reaction sometimes brings about the replacement of the diazo-group by hydrogen, sometimes by ethoxyl, or some similar oxy-radicle. (See also Hofmann, this vol., p. 1314).

L. T. T.

**Behaviour of Aldehyde, Glucose, Peptone, Albuminous Bodies, and Acetone towards Diazobenzenesulphonic Acid.** By PETRI (*Zeit. Phys. Chem.*, **8**, 291—298).—An alkaline solution of diazobenzenesulphonic acid added to the aldehydes of the fatty series or to glucose dissolved in weak alkali, produces a beautiful magenta-red reaction on standing 10 or 20 minutes; warming the solution hastens its appearance; it is only the fixed alkalis that can be used. The intensity of the colour depends very much on the proportion of the reagents; too much aldehyde or diazo-acid causes the

colour to disappear. Concentrated solutions absorb all the light, except the red end of the spectrum as far as C. On dilution, the absorption becomes less, only extending to D, while at the same time a clearing takes place in the blue between F and G. If cautiously neutralised either with mineral or organic acids, the colour disappears, but reappears again quite unchanged in properties on adding alkali; addition of an excess of mineral acid likewise produces a red colour, although differing in spectroscopic properties from the original. All attempts to separate the colouring matter with the usual solvents have failed. Bromine, chlorine, iodine, sulphurous and nitrous acids, together with sodium amalgam and zinc-dust (the last two when air is excluded), decolorise the red solution. If the sodium amalgam or zinc is filtered off and the filtrate exposed to the air, the colour reappears.

Aqueous solutions of peptone or albuminous bodies produce an orange-yellow to an orange-red colour with the alkaline diazo-acid, but it differs from the colour above described in both spectroscopic properties and its behaviour towards acids. When neutralised carefully, the orange-red is changed to yellow, but the colour does not reappear when an excess of mineral acid is employed. *Ammonia*, as well as fixed alkalis, reproduce it. When subjected to reduction with sodium amalgam or zinc-dust with access of air, a magenta-red colour is produced, which does not differ in any of its properties from the colour in the aldehyde reaction. Acetone, too, behaves like the aldehydes.

J. P. L.

**Action of Phenylhydrazine on the Imido-ethers.** II. By A. PINNER (*Ber.*, 17, 2002—2004).—In the first part of this paper (this vol., p. 743), the author described the formation of benzenyldiphenylazidine from phenylhydrazine and benzimido-ether hydrochloride. *Methenyldiphenylazidine*,  $\text{NHPh.N}:\text{CH.N}_2\text{H}_2\text{Ph}$ , is prepared by adding phenylhydrazine to a solution of formimido-ether hydrochloride in absolute alcohol, and allowing the mixture to stand for some weeks. It crystallises in yellow plates, melts at  $185^\circ$ , is soluble in hot benzene, sparingly soluble in cold, readily soluble in hot alcohol, and gives a deep-red coloration with hydrochloric or sulphuric acid. The yield is not good, resinous products being largely formed.

With acetimido-ether, the reaction takes a different course, the product being *ethenyldiphenylazidine hydrochloride*,  $\text{NH}:\text{CMe.N}_2\text{H}_2\text{Ph.HCl}$ . It crystallises in long colourless prisms, containing  $\frac{1}{2}$  mol. or  $1\frac{1}{2}$  mol.  $\text{H}_2\text{O}$ , accordingly as it is crystallised from hot or cold alcohol. It is readily soluble in alcohol, insoluble in ether and benzene. It commences to decompose at  $150^\circ$ .

A. J. G.

**Derivatives of Benzylidene-phenylhydrazine.** By V. SCHROEDER (*Ber.*, 17, 2096—2098).—*Acetobenzylidene-phenylhydrazine*,



is obtained by dissolving benzylidenephénylhydrazine in acetic chloride and pouring the solution into water, or better by boiling the hydrazine with  $1\frac{1}{2}$ —2 parts of acetic anhydride and excess of sodium

acetate for about three hours, the product being poured into water, and the crystalline mass that separates carefully washed with water, and recrystallised from dilute alcohol. It forms long colourless needles which melt at  $115^{\circ}$ . It is insoluble in cold water, soda, ammonia, and hydrochloric acid. It dissolves in sulphuric acid, the solution acquiring an odour of bitter almonds; addition of water reprecipitates the substance apparently unchanged.

*Metanitrobenzylidene-phenylhydrazine*, obtained by heating phenylhydrazine with metanitrobenzaldehyde, forms red needles and melts at  $121^{\circ}$ . Its *acetyl compound*,  $C_{15}H_{13}N_3O_3$ , closely resembles the acetyl compound described above, and is prepared in a similar manner; it crystallises in yellow needles which melt at  $170^{\circ}$ .

Benzylidine-aniline does not yield an acetyl compound when treated with acetic chloride or anhydride.

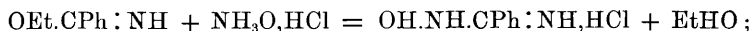
A. J. G.

**Action of Benzoic Chloride on Amidines.** By A. PINNER (*Ber.*, 17, 2004—2006).—By the action of benzoic chloride on benzamidine hydrochloride at  $120$ — $140^{\circ}$  there were obtained cyaphenine and dibenzamide in small quantity, the main product of the reaction being a substance of the empirical formula  $C_7H_7NO$ , isomeric or polymeric with benzamide. It melts with decomposition at  $230^{\circ}$ , benzonitrile being one of the products. It is being examined further.

The substance of the formula  $C_{14}H_{11}NO_2$ , obtained by Pinner and Klein by the action of fuming sulphuric acid on benzonitrile diluted with benzene, and termed by them benzimido-benzoate, is in reality dibenzamide.

A. J. G.

**Structure of Hydroxylamine-derivatives.** By W. LOSSEN (*Ber.*, 17, 1587—1589).—The author refers to a previous paper (*Ber.*, 16, 873), in which it is assumed that the action of hydroxylamine on acid chlorides is different from that of ammonia; and that benzhydroxamic acid, obtained from benzoic chloride and hydroxylamine, no longer contains the benzoic radical, but that its formula is  $OH.CPh:NOH$ . In like manner, ethylbenzhydroxamic acid may be represented by the formula  $OEt.CPh:NOH$ . This last formula is assigned by Pinner (this vol., p. 739) to his benzoximido-ether, obtained by the action of hydroxylamine hydrochloride on benzimido-ether. The author has compared the two substances, and finds that they are identical. The product of the action of benzimido-ether on hydroxylamine hydrochloride contains  $\alpha$ - and  $\beta$ -ethylbenzhydroxamic acids, which may be separated by partially neutralising with potash, and agitating with ether; this extracts the  $\beta$ -modification, whilst the  $\alpha$ -acid remains behind as potassium salt. Another substance,  $C_7H_8N_2O$ , is also produced, the formation of which may be expressed thus:



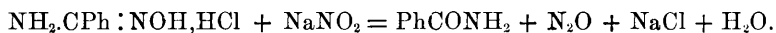
it resembles, and is perhaps identical with, the compound obtained by Tiemann (this vol., p. 734) from hydroxylamine and benzonitrile, and also with that obtained by Pinner (this vol., p. 739) by the action of hydroxylamine on benzamidine. It melts at about  $76$ — $77^{\circ}$ .

A. K. M.



**Remarks on the Previous Communication.** By A. PINNER (*Ber.*, 17, 1589—1590).—In reply to Lossen (see preceding Abstract), the author points out that the method of acting on hydroxylamine with benzimido-ether as modified by that chemist, is not favourable to the formation of benzoximido-ether, and he is of opinion that this is not identical with ethylbenzhydroxamic acid, but that it may possibly be readily converted into the latter. A. K. M.

**Amidoximes and Azoximes.** By F. TIEMANN and P. KRÜGER (*Ber.*, 17, 1685—1698).—The following experiments were undertaken to decide whether the compounds obtained by the action of hydroxylamine on the acid nitriles are oxamidines,  $\text{NH}:\text{CR}.\text{NH}.\text{OH}$ , or amidoximes,  $\text{NH}_2.\text{CR}:\text{N}.\text{OH}$  (see this vol., p. 734). The preparation of the compound  $\text{C}_7\text{H}_8\text{N}_2\text{O}$ , from benzonitrile and hydroxylamine, has already been described; it melts at  $79-80^\circ$ , and not at  $70^\circ$  as previously stated. It yields well-crystallised salts both with acids and alkalis, and like hydroxamic acid has a tendency to form acid salts of the alkali-metals; the hydrochloride has the formula  $\text{C}_7\text{H}_8\text{N}_2\text{O}.\text{HCl}$ . When a solution of the compound  $\text{C}_7\text{H}_8\text{N}_2\text{O}$  in alcoholic potash is warmed with a few drops of chloroform, the isonitrile odour is momentarily produced, and is succeeded by that of benzonitrile, the decomposition then proceeding further. The above compound combines with carbanil to form a carbamide, and with phenyl isothiocyanate to form a thiocarbamide. When sodium nitrite solution is added to a solution of the hydrochloride, nearly pure nitrous oxide is evolved, benzamide being simultaneously produced:



All these reactions indicate the presence of the group  $\text{NH}_2$  and the constitution  $\text{NH}_2.\text{CPh}:\text{NOH}$  (*benzenylamidoxime*). If, however, the conditions of the last experiment be modified, an excess of nitrite and a higher temperature being employed, and the solution slightly acidified, the decomposition goes further, some nitrogen is given off, and a small quantity of benzoic acid is also produced. The methyl-ether of benzenylamidoxime,  $\text{NH}_2.\text{CPh}:\text{NOMe}$ , is readily obtained by heating a solution of benzenylamidoxime, sodium methylate, and methyl iodide in methyl alcohol for some hours at  $100^\circ$ ; the greater part of the alcohol is then evaporated, and the methyl-derivative precipitated by water. It dissolves sparingly in cold, more readily in hot water, and is readily soluble in alcohol and ether; it melts at  $57^\circ$ , boils above  $230^\circ$ , and has basic but no acid properties. By the action of sodium nitrite on the hydrochloride, nitrogen is evolved, and a compound,  $\text{C}_6\text{H}_5\text{NO}_2$ , produced:  $\text{NH}_2.\text{CPh}:\text{NOMe}.\text{HCl} + \text{NaNO}_2 = \text{OH}.\text{CPh}:\text{NOMe} + \text{NaCl} + \text{N}_2 + \text{H}_2\text{O}$ ; the product,  $\text{OH}.\text{CPh}:\text{NOMe}$ , is named the methyl ether of *benzhydroxamic acid*, this being isomeric with Lossen's benzhydroxamic acid,  $\text{COPh}.\text{NH}.\text{OH}$ . It is an oil boiling at  $225^\circ$ , is insoluble in water, but readily soluble in alcohol, ether, and chloroform; it has neither basic nor any pronounced acid properties. When benzenylamidoxime is treated with water and sodium-amalgam, ammonia and benzaldehyde are readily detected by

their odour. On warming the liquid, an oil separates, the quantity of which is increased on neutralising with hydrochloric acid; it is readily soluble in hydrochloric acid, the solution yielding benzaldehyde when heated. This product is no doubt the benzaldoxime prepared by Petraczek (Abstr., 1883, 569), its formation being expressed thus:  $\text{NH}_2.\text{CPh}:\text{NOH} + \text{H}_2 = \text{CHPh}:\text{NOH} + \text{NH}_3$ . Secondary products are also formed. Benzenylamidoxime is identical with the compound obtained by Pinner from hydroxylamine and benzenylamidine hydrochloride (this vol., p. 739), and with the secondary product,  $\text{C}_7\text{H}_8\text{N}_2\text{O}$ , obtained by Lossen by the action of hydroxylamine hydrochloride on benzimido-ether (this vol., p. 1324). The above facts show that the addition-product from hydroxylamine and benzonitrile is an amidoxime, and therefore that the compounds obtained by the action of hydroxylamine on nitriles in general are to be regarded as belonging to this class of compounds. By the action of benzenylamidoxime on benzoic chloride, *benzoylbenzenylamidoxime*,  $\text{NH}_2.\text{CPh}:\text{NOBz}$ , is obtained crystallising in slender white needles; it melts at  $140^\circ$ , is insoluble in water, readily soluble in alcohol, ether, and benzene; it shows basic but no acid properties. When heated above its melting

point, water is given off, and *dibenzenzylazoxime*,  $\text{N} \begin{array}{c} \diagup \text{CPh} \diagdown \\ \diagdown \text{O.CPh} \diagup \end{array} \text{N}$ , is pro-

duced. This is an indifferent and very stable compound, insoluble in dilute acids and in alkalis; its solutions in concentrated nitric and sulphuric acids may be heated without decomposition; by continued boiling with tin and hydrochloric acid, it is reduced to benzonitrile. Dibenzenzylazoxime is almost insoluble in water, readily soluble in alcohol, ether, and benzene, melts at  $108^\circ$ , and boils at  $290^\circ$ ; it is readily volatile in steam, and forms long white needles on sublimation. It is also formed on heating benzenylamidoxime with benzoic chloride, benzotrichloride, or benzoic acid, and in all reactions in which benzoic acid is formed by the partial decomposition of benzenylamidoxime at a moderately high temperature, as, for example, by the action of

nitrous acid. *Benzenylazoximethenyl*,  $\text{N} \begin{array}{c} \diagup \text{CPh} \diagdown \\ \diagdown \text{O.CMe} \diagup \end{array} \text{N}$ , obtained by boil-

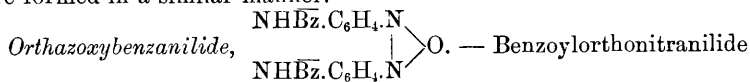
ing benzenylamidoxime with acetic anhydride, crystallises in flat prisms, sublimes at ordinary temperatures, and is readily volatile in steam; it melts at  $41^\circ$ , dissolves sparingly in water, but readily in alcohol, ether, and benzene. An isomeric *ethenzylazoximebenzenyl*,

$\text{N} \begin{array}{c} \diagup \text{CMe} \diagdown \\ \diagdown \text{O.CPh} \diagup \end{array} \text{N}$ , melting at  $57^\circ$ , has been prepared by Nordmann from

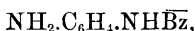
ethenzylamidoxime (from acetonitrile). In naming the azoximes which contain two different hydrocarbon radicles, that which is united to the oxygen-atom is placed at the end of the name as in the above examples. Benzenylazoximethenyl, which appears to be produced by the action of chloroform on an alkaline solution of benzenylamidoxime, is likewise to be distinguished from methenzylazoximebenzenyl, which should result from the action of benzoic chloride on methenzylamidoxime,  $\text{NH}_2.\text{CH}:\text{NOH}$ .

A. K. M.

**Reduction of Benzoylorthonitranilide.** By W. G. MIXTER (*Amer. Chem. J.*, **6**, 26—28).—Hübner (*Ann. Chem.*, **208**, 302), by the action of tin and hydrochloric acid on benzoyl-*o*-nitranilide, obtained benzenylphenylenamidine,  $C_{13}H_{10}N_2$ ; other reduction-products have not been prepared. The para- and meta-nitranilides, when treated with zinc and ammonia, yield azo- and amido-derivatives (this vol., p. 665); it is now shown that analogous ortho-compounds are formed in a similar manner.



is dissolved in alcohol, and zinc, ammonia, and platinic chloride added. The new compound slowly separates from the solution. It is yellow, sparingly soluble in alcohol, and melts at  $195^\circ$ . If the mother-liquor is evaporated to dryness, and the residue extracted with boiling water, it gives, on cooling, crystals of *benzoylorthophenylenediamine*,



melting at  $140^\circ$ . It is more easily obtained by reducing benzoylorthonitranilide with alcoholic ammonium sulphide. The platinichloride is a slimy precipitate. During the reduction with zinc and ammonia, some benzenylphenylenamidine is formed. H. B.

**Nitrosophenols.** By H. GOLDSCHMIDT and H. SCHMID (*Ber.*, **17**, 2060—2065).—To test the general applicability of the method of formation of nitrosophenols by the action of hydroxylamine on quinones (Goldschmidt, this vol., p. 735), the authors now apply the reaction to thymoquinone, toluquinone, and  $\alpha$ -naphthaquinone.

Thymoquinone is reduced by free hydroxylamine to hydrothymoquinone; hydroxylamine hydrochloride, on the other hand, converts it into nitrosothymol. Unsuccessful attempts were made to convert thymoquinone into a di-isonitroso-compound.

Toluquinone, dissolved in 200 times its weight of water mixed with hydroxylamine hydrochloride, and allowed to remain for 24 hours, yields white needles of *nitroso-orthocresol*,

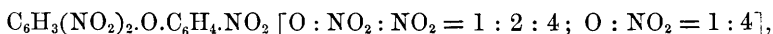


It decomposes between  $130$ — $140^\circ$ , gives Liebermann's nitroso-reaction, dissolves in alkalis with reddish-brown colour, and is converted into dinitro-orthocresol by treatment with nitric acid.

$\alpha$ -Naphthoquinone, when treated with hydroxylamine hydrochloride, is converted into  $\alpha$ -nitroso- $\alpha$ -naphthol. This substance, when pure, decomposes *without fusion* at  $190^\circ$ ; it is generally stated to melt at  $175^\circ$ . The authors did not succeed in replacing the second oxygen-atom in  $\alpha$ -naphthaquinone by an isonitroso-group. These and the earlier results obtained show that in all quinones 1 oxygen-atom can be replaced by the oximido-group, but that both oxygen-atoms can only be so replaced in those quinones in which both CO-groups are in the ortho-position. A. J. G.

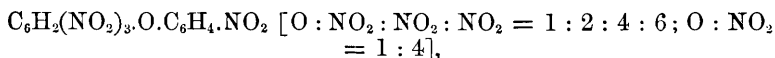
**Para- and Ortho-nitrophenyl Ethers of Dinitrophenol and of Picric Acid.** By C. WILLGERODT and E. HUETLIN (*Ber.*, **17**, 1764—1766).—These four ethers were prepared by the action of alcoholic solutions of  $\alpha$ -dinitrochlorobenzene and of picryl chloride (trinitrochlorobenzene) on potassium para- and ortho-nitrophenate. In the case of the two ethers from  $\alpha$ -dinitrochlorobenzene, heating in closed tubes for 5—6 hours at 150—160° was necessary: the derivatives of picric acid were easily prepared by digestion on the water-bath. In the preparation of the potassium phenates, care must be taken not to add excess of potash, or the ethyl ethers will also be formed.

*$\alpha$ -Dinitrophenyl paranitrophenyl oxide,*



crystallises from water in hexagonal plates melting at 114°, and soluble in ether, benzene, glacial acetic acid, and acetone.  *$\alpha$ -Dinitrophenyl orthonitrophenyl oxide* crystallises in minute needles melting at 119°. It resembles the para-derivative in solubility, &c.

*Trinitrophenylparanitrophenyl oxide,*



crystallises in small, thin, transparent, colourless scales which melt at 153°, and are easily soluble in alcohol, chloroform, benzene, glacial acetic acid, and acetone; more sparingly in ether and light petroleum. *Trinitrophenyl orthonitrophenyl oxide* crystallises from alcohol in small and almost colourless needles which melt at 172—173°, and resemble the para-compound in solubility, &c. L. T. T.

**Mercaptans.** By O. STADLER (*Ber.*, **17**, 2075—2081).—From the analogy in behaviour between mercaptans and phenols, it seemed probable that the mercaptans of the fatty group might, like the phenols, yield azo-compounds by reaction with diazo-compounds. The author's results show that not azo- but diazo-compounds are formed.

By the action of diazobenzenesulphonic acid on ethyl mercaptan suspended in ice-water and mixed with soda, a substance of the formula  $\text{C}_6\text{H}_5\text{N}_2\text{S}_2\text{O}_3\text{Na}$  (probably  $\text{SO}_3\text{Na} \cdot \text{C}_6\text{H}_4 \cdot \text{N}=\text{N} \cdot \text{SEt}$ ), is obtained, crystallising in clear yellow needles. It explodes when heated on platinum-foil; by boiling in alcoholic solution, nitrogen is evolved and the sulphonic acid of ethyl phenyl sulphide is formed. The sodium salt,  $\text{SO}_3\text{Na} \cdot \text{C}_6\text{H}_4 \cdot \text{SEt}$ , crystallises in white plates. Distilled with ammonium chloride, it yields ethyl phenyl sulphide.

Diazobenzene chloride and ethyl mercaptan reacted, giving an oily product, which, after extraction with ether, &c., proved to be a mixture of ethyl bisulphide and ethyl phenyl sulphide. On repeating this experiment, however, the ethereal solution exploded with considerable violence, showing that an unstable nitrogen-compound had been formed, but its isolation could not be effected.

Phenyl mercaptan is conveniently prepared by distilling a mixture

of sodium benzenesulphonate and potassium hydrosulphide in a vacuum.  
A. J. G.

**Bromoparaxylenol.** By P. ADAM (*Bull. Soc. Chim.*, **41**, 288—289).—When this compound is prepared by the ordinary method, condensation-products are formed which render the purification of the brominated derivative extremely difficult. It may be readily prepared by the action of bromine on xylenol heated to 160°; the source of heat is removed and the bromine is introduced rapidly (30 grams per minute). The solid product is purified by distilling with steam, or better, by exposing it in a vacuum, then washing with a little light petroleum and pressing between paper. It crystallises in white needles insoluble in water, but soluble in half their weight of boiling alcohol; they melt at 74°. When boiled with a large excess of water, bromoparaxylenol is decomposed, hydrobromic acid is evolved, and a substance remains in solution which is deposited when the liquid is evaporated in a vacuum. The author is continuing the study of the derivatives of this compound.  
W. R. D.

**Derivatives of Dimethylquinol.** By A. BAESSLER (*Ber.*, **17**, 2118—2129).—*Amidodimethylquinol*,  $C_6H_3(OMe)_2NH_2$  (comp. Mühlhauser, *Abstr.*, 1882, 302). Sodium-amalgam is gradually added to an alcoholic solution of nitrodimethylquinol, acidulated with acetic acid, until red needles are deposited on the sides of the vessel. The alcohol is then evaporated, water added, and the liquid extracted with ether. On evaporation, the ethereal solution leaves a mixture of red and yellow crystals which are boiled with very dilute alcohol; this leaves a residue consisting of azodimethylquinol mixed with small quantities of hydrazodimethylquinol. The solution contains amidomethylquinol, which is purified by crystallisation, conversion into the hydrochloride, &c. Amidodimethylquinol crystallises in nacreous plates, melts at 81—82°, is sparingly soluble in cold, soluble in hot water, alcohol, benzene, light petroleum, and carbon bisulphide. It is very unstable, being readily decomposed when heated above the melting point, and partially also by evaporating its aqueous solution. The hydrochloride crystallises in white efflorescent needles. The platinochloride is obtained as a brown precipitate.

*Acetamidodimethylquinol*,  $C_6H_3(OMe)_2NH\bar{A}c$ , obtained by the action of acetic anhydride on the base, crystallises in silvery white plates and melts at 91°. *Nitroacetamidodimethylquinol*,



obtained by adding fuming nitric acid, drop by drop, to a saturated aqueous solution of the acetyl-compound, crystallises in nodular groups of needles and melts at 164°.

*Dimethylquinoltrimethylammonium iodide*,  $C_6H_3(OMe)_2.NMe_3I$ , is prepared by heating amidodimethylquinol with methyl iodide and a little methyl alcohol in sealed tubes at 150° for five hours. It crystallises in white needles, melts at 202°, is readily soluble in water and dilute alcohol, nearly insoluble in benzene, chloroform, and light

petroleum, sparingly soluble in absolute alcohol. By the action of moist silver oxide, it is converted into the corresponding *hydroxide*, which crystallises in colourless needles. The *chloride*,



crystallises in needles, melts at  $172^\circ$ , and is readily soluble in water. The *platinochloride*,  $[\text{C}_6\text{H}_3(\text{OMe})_2\text{NMe}_3\text{Cl}]_2.\text{PtCl}_4$ , is a yellow crystalline substance.

By the action of phenyl isothiocyanate on amidodimethylquinol, a compound of the formula  $\text{NHPh.CS.NH.C}_6\text{H}_3(\text{OMe})_2$  is obtained, crystallising in white, microscopic needles, and melting at  $137^\circ$ ; it is readily soluble in hot benzene and alcohol, insoluble in water.

*Dimethylquinol-thiocarbamide*,  $\text{CS}[\text{NH.C}_6\text{H}_3(\text{OMe})_2]_2$ , is prepared by digesting amidodimethylquinol, alcoholic potash, and carbon bisulphide for some hours on the water-bath; it crystallises in white microscopic needles, melts at  $109^\circ$ , is readily soluble in hot alcohol, benzene, and chloroform, sparingly in light petroleum, and insoluble in water.

*Azodimethylquinol*,  $\text{N}_2[\text{C}_6\text{H}_3(\text{OMe})_2]_2$ , is prepared from an alcoholic solution of nitrodimethylquinol by the action of sodium-amalgam in presence of a small amount of ammonia, or by the action of zinc and potash. It is separated from the hydrazodimethylquinol simultaneously formed, by heating it with dilute hydrochloric acid, in which the hydrazo-compound dissolves completely. The azoquinol crystallises in red needles, melts at  $140^\circ$ , is readily soluble in absolute alcohol, benzene, chloroform, carbon bisulphide, and aniline, more sparingly in light petroleum and dilute alcohol, and is nearly insoluble in water. It dissolves without decomposition in strong hydrochloric acid with deep blue colour, and in concentrated sulphuric acid with violet colour; the latter solution suffers partial decomposition on standing, turning first blue and then green. By the action of bromine on an alcoholic solution of the azo-compound, *dibromazodimethylquinol*,  $\text{C}_{16}\text{H}_{16}\text{Br}_2\text{N}_2\text{O}_4$ , is obtained. It forms a red crystalline mass, melts at  $220^\circ$ , is soluble in benzene, chloroform, and carbon bisulphide, very sparingly in alcohol, and is insoluble in water. It dissolves in sulphuric acid without decomposition to form a deep-violet solution.

The hydrazo-compound could not be isolated; in solution it oxidises with great readiness to form the azo-compound.

*Tetramethoxydiamidodiphenyl*,  $\text{NH}_2.\text{C}_6\text{H}_2(\text{OMe})_2.\text{C}_6\text{H}_2(\text{OMe})_2.\text{NH}_2$ , is obtained as hydrochloride by the action of hydrochloric acid on solutions of the hydrazo-compound, and by the action of stannous chloride and hydrochloric acid on the azo-compound. The free base crystallises in snow-white needles, melts at  $210^\circ$ , is easily soluble in chloroform, carbon bisulphide, hot benzene, and boiling alcohol, but only sparingly in light petroleum or water. The hydrochloride,



crystallises in stellate groups of small white needles, and is readily soluble in water. The *platinochloride*,  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_4.\text{H}_2\text{PtCl}_6$ , is obtained as a yellow precipitate. The phenylthiocarbamide-derivative,



forms white flocks, melts at  $184^{\circ}$ , is soluble in alcohol and benzene, insoluble in light petroleum and water. The diacetyl-derivative,  $C_{12}H_4(OMe)_4(NHAc)_2$ , crystallises in white needles, melts at  $251^{\circ}$ , is readily soluble in alcohol, benzene, chloroform, and carbon bisulphide, but only very sparingly in light petroleum or water. A. J. G.

**Compounds of Phenols with Ethyl Acetoacetate.**  $\beta$ -Methylumbelliferone II. By H. v. PECHMANN and J. B. COHEN (*Ber.*, **17**, 2129—2138).—In the first communication on this subject (v. Pechmann and Duisberg, this vol., p. 66), a series of compounds were described, obtained by the action of phenols on ethyl acetoacetate in presence of sulphuric acid. These compounds were regarded as coumarins, or hydroxycoumarins, in which substitution had occurred in the side-chains. In particular, the compound derived from resorcinol showed such strongly-marked analogy with the hydroxycoumarin, umbelliferone, that it was termed  $\beta$ -methylumbelliferone, and had

assigned to it the constitution 
$$\text{OH.C}_6\text{H}_3 \begin{array}{l} \text{CMe:CH} \\ | \text{ (1)} \\ \text{O—CO} \\ \text{ (2)} \end{array} \text{ (4)}$$
. This view,

although opposed to that of Willenberg (*Abstr.*, 1882, 1289) and of Michael (this vol., p. 736), is confirmed by the results now brought forward.

*Allyl resorcinol methyl ether*,

$C_6H_3(OH)(OMe).CMe:CH_2$  [ $OH:OMe:C_2MeH_2 = 2:4:1$ ],

isomeric with eugenol, is obtained by heating umbellic acid. It forms a nearly colourless thick oil, of agreeable odour, distils at  $245\text{--}250^{\circ}$ , is insoluble in water, but miscible with most other solvents. Concentrated sulphuric acid dissolves it with red coloration. It is soluble in aqueous soda, but not in sodium carbonate.

*Methylic dimethyl- $\beta$ -methylumbellate* is obtained by heating the monomethyl acid with methyl iodide and sodium methylate in sealed tubes for five hours at  $90^{\circ}$ . The *free acid*,

$C_6H_3(OMe)_2.CMe:CH.CO_2H$  [ $4:2:1$ ],

crystallises in small colourless needles, melts at  $145^{\circ}$ , is insoluble in water, readily soluble in ether, benzene, alcohol, and chloroform. A solution of the ammonium salt gives a white curdy precipitate with lead acetate, a clear green precipitate with copper sulphate, and a yellow amorphous precipitate with ferric chloride. The silver salt forms a white granular powder. The *methyl salt*,

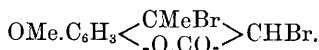
$C_6H_3(OMe)_2.CMe:CH.CO_2Me$ ,

is an oil boiling at  $310\text{--}320^{\circ}$ , and soluble in the ordinary solvents. By oxidation with an alkaline solution of potassium permanganate, it is converted into dimethyl- $\beta$ -resorecylic acid. This acid was shown by Tiemann and Will (*Ber.*, **15**, 2080) to be formed by the oxidation of umbelliferone, thus proving the side-chains in these compounds to occupy the same positions as in umbelliferone.

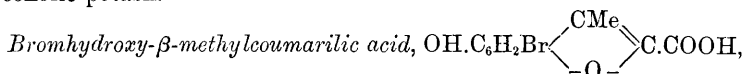
The authors regard Michael's tribromo-derivative, obtained by the action of bromine on  $\beta$ -methylumbelliferone, as  $\beta$ -methylbromumbelli-

*ferone dibromide*. They have only to add to Michael's description that it gives a violet coloration with dilute soda.

*β-Methylumbelliferone dibromide methyl ether*,



The action of bromine on the methyl ether differs slightly from that on *β*-methylumbelliferone, an additive product being obtained. It crystallises in colourless needles, melts at 233–235°, is insoluble in water, somewhat soluble in alcohol, ether, chloroform, and glacial acetic acid. Both bromine-atoms are removed by boiling it with alcoholic potash.



is obtained by boiling the tribromo-compound with alcoholic potash. It forms slender colourless needles, melts with decomposition at 221°, is readily soluble in alcohol, ether, and chloroform, sparingly in benzene, insoluble in water. It dissolves in sulphuric acid to a colourless solution, which turns purplish-violet on heating. Ferric chloride gives a yellow coloration. When the silver salt is distilled, it yields a crystalline substance, probably *bromhydroxy-β-methylcoumarone*; this yields a deep blue-coloured body by the action of gentle oxidising agents.

*Methoxy-β-methylhydrocoumaric anhydride*,  $\text{C}_{22}\text{H}_{22}\text{O}_6$ , is obtained by the action of sodium-amalgam on a solution of *β*-methylumbelliferone methyl ether in dilute alcohol. It crystallises in nearly colourless prisms, melts at 243–244°, is soluble in hot glacial acetic acid, insoluble in alcohol and ether. Sulphuric acid dissolves it, with feeble blue fluorescence. Soda only dissolves it on boiling.

*Nitro-β-methylumbelliferone*,  $\text{C}_{10}\text{H}_7(\text{NO}_2)\text{O}_3$ , is prepared by adding the calculated quantity of nitric acid, drop by drop, to the finely divided *β*-methylumbelliferone suspended in glacial acetic acid, and well cooled. It crystallises in straw-yellow needles, is insoluble in water, sparingly soluble in alcohol, benzene, and glacial acetic acid.

*Dinitro-β-methylumbelliferone*,  $\text{C}_{10}\text{H}_6(\text{NO}_2)_2\text{O}_3$ , is prepared by the action of excess of nitric acid on *β*-methylumbelliferone suspended in acetic acid, the mixture being finally heated on the water-bath. It crystallises in lustrous golden-yellow needles, melts at 220°, is readily soluble in alcohol and glacial acetic acid, sparingly in chloroform, benzene, and carbon bisulphide.

*Amido-β-methylumbelliferone*,  $\text{C}_{10}\text{H}_7\text{O}_3\text{NH}_2$ , is prepared by the action of tin and hydrochloric acid on the mononitro-compound. It forms yellowish needles, melts at 247°, is sparingly soluble in the ordinary solvents, and gives an intense green coloration with ferric chloride. The sulphate,  $(\text{C}_{10}\text{H}_9\text{NO}_3)_2\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$ , is very sparingly soluble in cold water.

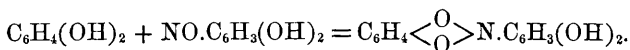
*Nitrosoamido-β-methylumbelliferone*,  $\text{C}_{10}\text{H}_6(\text{NO})\text{O}_3\text{NH}_2$ , is obtained by the action of nitrous acid on the sulphate of the amido-derivative. It crystallises in yellowish-red needles, melts at 140°, is readily soluble in alcohol, sparingly in water, ether, benzene, and chloroform. It has no basic properties, is soluble in alkalis, with deep red colour,



is not decomposed by boiling with acids, and gives Liebermann's reaction.

A. J. G.

**Azoresorcinol and Azoresorufin.** By H. BRUNNER and C. KRAEMER (*Ber.*, **17**, 1847—1866).—In a preliminary notice (*Abstr.*, 1882, 784), H. Brunner stated that by acting with sulphuric acid on a mixture of nitrobenzene and resorcinol, he had obtained a colouring matter which he believed to be identical with the diazoresorufin described by Weselsky (*Ber.*, **4**, 614). In conjunction with C. Krämer, he has now carefully compared these two substances, and proved the correctness of his surmise. This body was prepared by Weselsky by heating his diazoresorcinol with sulphuric acid at  $210^{\circ}$ ; by Liebermann (*this Jour.*, 1874, 693) by heating resorcinol with sulphuric acid containing nitrous acid; by Bindschedler and Busch, and also by Fèvre, from nitrosoresorcinol (from amyl nitrite and sodium resorcinol) and sulphuric acid. When prepared by Brunner's method, the substance in question is always accompanied by paramidophenolsulphonic acid (see p. 1354) in the form of white silky needles. The mixed compounds are dissolved in hot ammonia, and hydrochloric acid is added to the still hot solution. Diazoresorufin is at once precipitated, and if the solution be not too concentrated, all the sulphonic acid remains in solution and crystallises out on cooling. The diazoresorcinol employed by Weselsky was obtained by acting on resorcinol with nitric acid saturated with nitrous anhydride. It forms deep green crystals, which dissolve in alkalis to a bluish-violet solution with brown fluorescence. Weselsky gave  $C_{15}H_{12}N_2O_6$  as the formula of this compound, but a careful re-examination by the author has proved that its true composition is  $C_{12}H_9NO_4$ , so that, taking into account its formation from nitrosoresorcinol, it may be looked upon as formed according to the reaction—



As it is not a diazo-compound, the author proposes to substitute the name *azoresorcinol* for diazoresorcinol, and in like manner diazoresorufin becomes *azoresorufin*.

*Azoresorufin* prepared by any of the above-mentioned methods has the formula  $C_{24}H_{16}N_2O_7$  ( $C_{36}H_{18}N_4O_2$ , Weselsky). It is a reddish-brown powder sparingly soluble in alcohol, insoluble in water and in ether. It dissolves in sulphuric acid to a blue solution containing a sulphonic acid, which is, however, decomposed by water. Alkalis convert it into a very intense brilliant carmine solution, having a vermilion fluorescence. This is an intensely strong colouring matter, and forms a valuable test for the presence of traces of alkali.

By the action of acetic chloride on azoresorcinol, Weselsky obtained a compound (crystallising in yellow scales) to which he ascribed the formula  $C_{48}H_{30}N_4Cl_5O_{15}$ , and which he regarded as hexacetyl-azoresorcinol, in which each of the four nitrogen-atoms is further combined with two chlorine-atoms. The authors have carefully examined this reaction, and have obtained two compounds. The one crystallises in small golden-yellow scales of the formula  $C_{12}H_8ClNO_3.HCl$ , and is not an acetyl-compound. The other compound forms a green amor-

phous mass easily soluble in ether. It gave results leading to the formula  $C_{26}H_{21}N_2Cl_3O_8$  (or  $C_{24}H_{14}EtClN_2O_8 \cdot 2HCl$ ). It is probable that here we have first the formation of a dihydrochloride of chlorazoresorufin monacetate, which in the process of purification with alcohol exchanges its acetyl-group for ethyl.

*Azoresorufin diacetate*,  $[C_6H_4O_2N \cdot C_6H_5(OAc)]_2$ , was obtained by digesting azoresorcinol with sodium acetate and acetic anhydride at  $135^\circ$ . It forms a yellowish-brown amorphous substance, easily soluble in acetone, chloroform, and acetic acid, sparingly in alcohol or ether. When evaporated with hydrochloric acid on the water-bath, it yields a yellow hydrochloride.

*Azoresorufyl hydrochloride*,  $C_{24}H_{11}Cl_2N_2O_5 \cdot 2HCl$ , was obtained by digesting azoresorcinol with fuming hydrochloric acid under pressure at  $100^\circ$ . It forms bluish-violet crystals.

Both azoresorcinol and azoresorufin yield identical products on reduction, either in acid or in alkaline solution. When azoresorcinol is reduced with tin and hydrochloric acid, a compound is formed which is soluble in dilute hydrochloric acid, and crystallises in iridescent scales. Its formula is  $C_{48}H_{46}N_4O_{13} \cdot 4HCl + 4H_2O$ . When quickly dried at  $100^\circ$ , it forms a blue powder which dissolves in boiling acetone or alcohol (if slightly acidulated with hydrochloric acid) with an indigo colour, and these solutions both yield large well-formed crystals very much resembling potassium permanganate in appearance. When once formed, these crystals redissolve with difficulty. Although exactly alike in appearance, analysis showed these two substances differed in the quantity of hydrochloric acid they contain. That crystallised from alcohol has the formula  $C_{48}H_{46}N_4O_{13} \cdot 3HCl$ , that from acetone,  $C_{48}H_{46}N_4O_{13} \cdot HCl$ . Hydrating agents (such as dilute alkalis) gradually convert these compounds, first into azoresorufin, then into azoresorcinol.

*Tetrahydroazoresorufin*,  $C_{24}H_{16}N_2O_7 \cdot H_4$ , is formed if azoresorcinol is subjected to reduction with zinc and hydrochloric acid. It crystallises in dark blue crystals with a strong coppery iridescence. At  $100^\circ$  it loses water, and is reconverted into azoresorufin. It forms a dihydrochloride yielding colourless crystals. The tetrahydro-compound is also formed when sulphuretted hydrogen is passed into an ammoniacal solution of resorufin. Sodium-amalgam seems to form a colourless leuco-compound, but this is so unstable that the authors have not succeeded in isolating it.

*Dibromazoresorcinol hydrobromide*,  $C_{12}H_7Br_2NO_4 \cdot HBr$ , is obtained by adding bromine to a solution of azoresorcinol in sodium hydroxide. It forms a glistening green mass soluble in alcohol to a blue liquid having a brownish-red fluorescence.

*Hexabromazoresorufin hydrobromide*,  $C_{24}H_{10}Br_6N_2O_7 \cdot HBr$ , is probably identical with the bromodiazoresorufin of Bindschedler and Busch, and of the Bavarian Aniline and Soda Works. It is obtained from resorufin in a manner similar to that by which the last-named compound is prepared from azoresorcinol. It is an amorphous red substance, soluble in alcohol to a violet liquid with a bluish-red fluorescence.

*Trinitrazoresorcinol*,  $C_{12}H_6(NO_2)_3NO_4$ , was obtained by nitration

with nitric acid of sp. gr. 1.37. Care must be taken in the nitration, or the substance will be completely oxidised. It forms green glistening crystals. This compound is probably what Weselsky described as tetrazoresorcinol nitrate, and to which he ascribed the formula  $C_{36}H_{12}N_8O_{12}, 6NO_3$ . It is soluble in water, ether, and alcohol, forming indigo-coloured solutions.

*Hexanitrazoresorufin*,  $C_{24}H_{10}(NO_2)_6N_2O_7$ , prepared in a similar manner, crystallises in small green needles, which dissolve in water, alcohol, and ether to purple solutions. L. T. T.

**Derivatives of Pyrogallol and Phloroglucinol, and their Relation to Daphnetin and Æsculetin.** By W. WILL and K. ALBRECHT (*Ber.*, 17, 2098—2109).—Whilst daphnetin was known to be a derivative of pyrogallol, it was still uncertain which of the two other trihydroxybenzenes æsculetin was derived from. The results given in the present paper show that it is not derived from phloroglucinol, and must therefore be derived from hydroxyquinol.

*Ethyl triethylgallate*,  $C_6H_2(OEt)_3.COOEt$ , is prepared by boiling ethyl gallate and ethyl iodide with potash. It crystallises in lustrous needles, melts at  $51^\circ$ , and is readily soluble in alcohol, ether, and benzene.

*Triethylgallic acid*,  $C_6H_2(OEt)_3.COOH$ , is obtained by saponification of the ethyl salt with alcoholic potash, and decomposition of the potassium salt formed with hydrochloric acid. It is crystalline, melts at  $112^\circ$ , is sparingly soluble in cold, more readily in boiling alcohol. It does not give a coloration with ferric salts. The neutral solution of the ammonium salt gives a clear greenish-blue precipitate with copper salts, white precipitates with lead and zinc salts. The silver salt,  $C_{13}H_{17}O_5Ag$ , is obtained by precipitation with silver nitrate as a voluminous white precipitate sparingly soluble in hot water, and can be crystallised from it. It melts at  $200^\circ$ , and decomposes into carbonic anhydride and pyrogallol triethyl ether.

*Ethyl pyrogallalcarboxylate*,  $C_6H_2(OH)_3.COOEt$ , obtained by saturating a solution of pyrogallalcarboxylic acid in alcohol with hydrochloric acid, forms a crystalline mass; when crystallised from hot water it unites with 1 mol. of  $H_2O$ , and then melts at  $86^\circ$ ; the anhydrous salt melts at  $102^\circ$ . It commences to sublime at  $100^\circ$ . It is soluble in alcohol and ether, insoluble in hot water. With ferric chloride, it gives a greenish-brown coloration like that produced by the free acid. By the action of ethyl iodide and potash, it is converted into *ethyl triethylpyrogallalcarboxylate*, a colourless, odourless, volatile oil, insoluble in water and alkalis, readily soluble in alcohol and ether.

*Triethylpyrogallalcarboxylic acid*,  $C_6H_2(OEt)_3.COOH$  [ $COOH : OEt : OEt = 1 : 2 : 3 : 4$ ], prepared from the ethyl salt, is crystalline, melts at  $100.5^\circ$ , and is identical with the triethoxybenzoic acid obtained from daphnetin. The silver salt,  $C_{13}H_{17}O_5Ag$ , is moderately soluble in water, and decomposes at  $130^\circ$  into carbonic anhydride and pyrogallol triethyl ether.

*Phloroglucinocarboxylic acid*,  $C_6H_2(OH)_3.COOH$ , is prepared by heating pure phloroglucinol (1 part), hydrogen potassium carbonate (4 parts), and water (4 parts) in sealed tubes for 13 hours at  $130^\circ$ .

The product of the reaction is treated with dilute hydrochloric acid and extracted with ether. The ethereal solution is next shaken with aqueous hydrogen sodium carbonate, whereby the acid passes into the aqueous solution, whilst unaltered phloroglucinol remains dissolved in the ether. The sodium carbonate solution is then acidified, the acid extracted with ether, and the ethereal solution allowed to crystallise. The free acid resembles gallic and pyrogallolcarboxylic acids in appearance and behaviour. It crystallises with 1 mol.  $\text{H}_2\text{O}$ , decomposes slowly when heated (even below  $100^\circ$ ), and finally melts at  $206^\circ$  (the melting point of phloroglucinol). The aqueous solution on boiling is completely decomposed into carbonic anhydride and phloroglucinol. An alkaline solution turns brown if exposed to the air. Ferric chloride gives an intense blue coloration, which soon turns to a dirty brown. An aqueous solution of the acid gives white precipitates with lead and silver salts.

In preparing this acid with phloroglucinol prepared from resorcinol there is obtained in addition another acid quite insoluble in water, and therefore readily separated from phloroglucinolcarboxylic acid. *Diresorcinoldicarboxylic acid*,  $\text{COOH} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{COOH}$ , obtained thus, is sparingly soluble in alcohol, more readily in ether. It decomposes above  $300^\circ$  without previous fusion. Diresorcinol when heated with hydrogen potassium carbonate, as described above, yields this acid exclusively. The potassium salt,  $\text{C}_{14}\text{H}_8\text{O}_8\text{K}_2$ , crystallises in slender white needles; the barium salt,  $\text{C}_{14}\text{H}_8\text{O}_8\text{Ba} + 6\text{H}_2\text{O}$ , forms lustrous needles; the silver salt,  $\text{C}_{14}\text{H}_8\text{O}_8\text{Ag}_2$ , is precipitated in white floes.

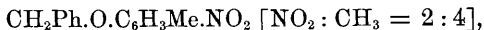
*Phloroglucinol diethyl ether*,  $\text{C}_6\text{H}_3(\text{OEt})_2\text{OH}$ .—By the action of hydrochloric acid gas on an alcoholic solution of phloroglucinolcarboxylic acid, there was obtained, not as was expected, the ethyl salt of the acid, but phloroglucinol diethyl ether, a substance crystallising in long colourless lustrous needles, and melting at  $75^\circ$ . It distils unaltered, is soluble in water or dilute alcohol, and is also readily soluble in alkalis, from which solution addition of acids reprecipitates it unchanged. It may also be prepared by the action of hydrochloric acid gas on an alcoholic solution of phloroglucinol. Attempts to prepare an ethylated phloroglucinol-carboxylic acid were unsuccessful.

*Phloroglucinol triethyl ether*,  $\text{C}_6\text{H}_3(\text{OEt})_3$ , is obtained by the action of ethyl iodide and alcoholic potash on phloroglucinol diethyl ether. It is crystalline, melts at  $43^\circ$ , can be distilled with steam, is readily soluble in alcohol and ether, insoluble in water and alkalis. It is not identical with the triethyl ether obtained by dry distillation of the calcium salt of the triethoxybenzoic acid derived from æsculetin. As the three triethoxybenzenes theoretically possible are now known, and as two of them are characterised as the triethyl ethers of pyrogallol and phloroglucinol respectively, it follows that the third must be the triethyl ether of hydroxyquinol.

This conclusion that æsculetin is not a phloroglucinol-derivative, is in agreement with the results lately obtained by v. Pechmann and Welsh (this vol., p. 1346).

A. J. G.

**Nitro-derivatives of Paracresyl Benzyl Ether.** By P. FRISCHE (*Annalen*, **224**, 137—155).—*Nitrocresyl benzyl ether*,



prepared by the action of potassium nitrocresol on benzyl chloride, crystallises in broad needles which dissolve in benzene, ether, light petroleum, and alcohol. The crystals melt at  $54^\circ$  and decompose when strongly heated.

*Dinitrocresyl benzyl ether*,  $\text{CH}_2\text{Ph.O.C}_6\text{H}_2(\text{NO}_2)_2\text{Me.NO}_2$ , can only be prepared by acting on silver dinitrocresol with benzyl iodide. It is deposited from hot alcohol in crystalline plates melting at  $109^\circ$ , which decompose on exposure to the light.

*Cresyl nitrobenzyl ether*,  $\text{C}_6\text{H}_4\text{Me.O.CH}_2\text{.C}_6\text{H}_4\text{.NO}_2$ , also crystallises in plates which melt at  $91^\circ$ .

*Nitrocresyl nitrobenzyl ether*,  $\text{NO}_2\text{.C}_6\text{H}_3\text{Me.O.CH}_2\text{.C}_6\text{H}_4\text{.NO}_2$ , forms silky needles which are soluble in benzene and hot acetic acid and melt at  $163^\circ$ .

*Dinitrocresyl nitrobenzyl ether*,  $\text{NO}_2\text{.Me(NO}_2)_2\text{C}_6\text{H}_2\text{.O.CH}_2\text{.C}_6\text{H}_4\text{.NO}_2$ , melts at  $186.5^\circ$  and dissolves in hot glacial acetic acid. It is not only formed by the actions of nitrobenzyl iodide on silver dinitrocresol, but also by the nitration of many of the above ethers.

Nitrocresyl benzyl ether, on nitration, yields nitrocresol and benzyl alcohol, which are further changed into dinitrocresol and nitrobenzyl nitrate, a small quantity of dinitrocresyl nitrobenzyl ether is also formed. Under similar treatment, the isomeric cresyl nitrobenzyl ether gives a much larger yield of dinitrocresyl nitrobenzyl ether. Dinitrocresol paranitrobenzyl nitrate and a large quantity of dinitrocresyl nitrobenzyl ether are obtained by the action of strong nitric acid on nitrocresyl nitrobenzyl ether.

Alcoholic ammonia acts slightly on nitrocresyl benzyl ether, and has no action on cresyl nitrobenzyl ether. It converts dinitrocresyl benzyl ether into dinitroparatoluidine and benzyl alcohol, and saponifies dinitrocresyl nitrobenzyl ether, forming nitrobenzyl alcohol and dinitrotoluidine.

Attempts to reduce these nitro-ethers to amido-compounds were unsuccessful.

W. C. W.

**Nitration of the Phenyl and Cresyl Ethers of Phosphoric Acid.** By M. RAPP (*Annalen*, **224**, 156—178).—When a solution of monophenylphosphoric acid in strong nitric acid is poured into water, the nitro-product is not precipitated, but on evaporating the mixture (after the addition of alcohol) to remove the excess of nitric acid, *mononitromonophenyl phosphate* is obtained in crystalline plates melting at  $112^\circ$ . The crystals are soluble in ether, benzene, chloroform, and in hot water. They are decomposed by potash, yielding paranitrophenol and potassium phosphate, and they are also decomposed by the prolonged action of nitric acid.

*Dinitrodiphenyl-phosphoric acid*,  $\text{PO(O.C}_6\text{H}_4\text{.NO}_2)_2\text{.OH}$ , prepared from diphenyl phosphate, crystallises in white needles melting at

133·5°, which are soluble in ether, benzene, and hot alcohol. If the crystals are mixed with the mononitro-derivative, they dissolve freely in cold chloroform.

*Trinitrotriphenyl phosphate*,  $\text{PO}(\text{O.C}_6\text{H}_4\text{NO}_2)_3$ , is deposited from hot acetic acid in oblique prisms which melt at 155° and are insoluble in the ordinary solvents. On decomposition with potash, the theoretical yield of paranitrophenol is obtained. This substance may with advantage be prepared by means of this reaction. Trinitrotriphenyl phosphate is converted into dinitrodiphenyl ethyl phosphate by prolonged boiling with alcohol. Trinitrotriphenyl phosphate has also been obtained by Engelhardt and Latschinoff (*Zeit. f. Chem.*, 1870, 230), by the action of phosphorus pentachloride on paranitrophenol.

*Monoparacresyl phosphate*,  $\text{PO}(\text{O.C}_6\text{H}_4\text{Me})(\text{OH})_2$ , forms white plates which melt at 116°, and dissolve freely in alcohol, ether, and water. Triparacresyl phosphate has been previously described by A. Wolkow (*ibid.*, 1870, 322), who found the melting point 8° too low, viz., 68° instead of 76°. No nitro-derivatives of these ortho- or para-cresyl phosphates could be obtained.

W. C. W.

**Hydroxydihydrocarbostyryl.** By A. EINHORN (*Ber.*, 17, 2011—2014).—*Hydroxydihydrocarbostyryl*,  $\text{C}_6\text{H}_4 \begin{matrix} \text{CH}(\text{OH})\cdot\text{CH}_2 \\ \diagdown \quad | \\ \text{N}=\text{C}\cdot\text{OH} \end{matrix}$ , the lac-

time of orthamidophenyllactic acid is prepared by the reduction of orthonitrophenyl-β-lactic acid or orthonitrophenyllactamide with ferrous hydroxide and ammonia. It crystallises with 2H<sub>2</sub>O in well-formed lustrous white needles, and is readily soluble in water, ether, and chloroform. The hydrated compound melts at 95–97°; after drying over sulphuric acid, it loses its water of crystallisation and then melts at 149°. It is converted into carbostyryl by heating it several times to the fusing point, or by adding a small quantity of acid or alkali to its aqueous solution, or even by boiling the solution for five minutes. It is isomeric with the hydroxyhydrocarbostyryl (m. p. 197–198°), obtained by Erlenmeyer and Lipp (*Abstr.*, 1883, 992) by the reduction of the nitration-products of phenyl-α-lactic acid.

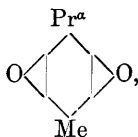
A. J. G.

**Safrole.** By J. SCHIFF (*Ber.*, 17, 1935–1940).—*Safrole* is the main constituent of the essential oil of sassafras (from *Laurus sassafras*). It crystallises at low temperatures (Arzruni, this Journal, 1877, ii, 202), melts at 8°, forms, at ordinary temperatures, a clear colourless oil of sharp taste; its sp. gr. 1·0956 at 18°. Is of neutral reaction, optically inactive, and boils at 232°. The author's analysis confirm the formula C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>, assigned to safrole by St. Evre (*Ann. Chim. Phys.* [3], 12, 107), and by Grimaux and Knotte (*Compt. rend.*, 68, 928). The oxygen-atoms in safrole would appear not to be present as hydroxyl, as neither hydrochloric acid nor phosphoric chloride converts it into a chlorine-derivative. Safrole is not affected by aqueous or alcoholic potash, and is only very slightly attacked by fusion with caustic potash, does not reduce ammoniacal silver solutions, does not unite with bisulphites, and is not acted on by

ammonia or nascent hydrogen. It is therefore neither an ethereal salt, an aldehyde, nor a ketone. A large number of reducing agents were tried but had no action on it. Heated for 24 hours with metallic sodium, it suffers no change beyond apparently partial polymerisation. Oxidation with nitric acid and with a saturated solution of potassium permanganate completely convert safrole into carbonic anhydride and oxalic acid. Dilute permanganate oxidises it to carbonic anhydride, oxalic acid, formic acid, propionic acid, and a small quantity of a neutral substance of the formula  $C_{10}H_{12}O_4$ , crystallising in microscopic rhombic prisms; this melts at  $59^\circ$ , decomposes on heating to  $120^\circ$ , is soluble in hot water, alcohol, ether, and in aqueous ammonia and potash; iodine completely decomposes safrole; chlorine converts it into a mixture of liquid chlorine-derivatives which decompose below  $100^\circ$  and could not be separated.

A. J. G.

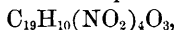
**Constitution of Safrole.** By T. POLECK (*Ber.*, **17**, 1940—1944).—From a consideration of the results detailed in the preceding paper, of the negative result of his own experiments with reducing agents, and of its indifference to hydroxylamine, the author considers that the constitution of safrole is best expressed by the formula



*i.e.*, as cymene in which four hydrogen-atoms have been replaced by oxygen. Measurements of the refractive index give results showing that probably either three or four carbon-atoms are in double union. At present there is no direct proof of the presence of the benzene-ring.

A. J. G.

**Salts and Ethers of Aurin and Rosolic Acid.** By E. ACKERMANN (*Ber.*, **17**, 1624—1627).—Graebe and Caro showed that, by treating aurin and rosolic acid with acetic anhydride, it cannot be proved that these substances contain two hydroxyl-groups; the author, however, proves this by means of salts and ethers. The *silver salt* of aurin, obtained by precipitating the ammonium salt, forms an insoluble brownish-red crystalline powder, apparently of no very definite composition; the *potassium salt* obtained by neutralising aurin with potash dissolves very readily in water, readily also in alcohol; it was found to contain 17.1 per cent. potassium, whilst the formula  $C_{19}H_{12}K_2O_3$  requires 21.3 per cent. On adding lead acetate to an ammoniacal solution of aurin, a reddish-brown basic salt,  $2C_{19}H_{12}O_3Pb + PbO$ , is precipitated. Better results are obtained with the nitro- and bromo-derivatives, these more negative compounds yielding salts of constant composition. *Tetranitro-aurin*,

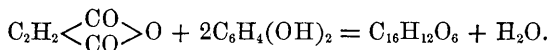


forms brownish-yellow microscopic needles which explode on heating; it melts at about  $140^\circ$ , is almost insoluble in water, benzene, chloroform, and ether, readily soluble in alcohol; alkalis and

alkaline carbonates dissolve it with dark-red coloration; the *barium salt* dried at  $150^{\circ}$  has the composition  $C_{19}H_8(NO_2)_4O_3Ba$ , and forms a black powder with greenish lustre; the *silver salt*,  $C_{19}H_8(NO_2)_4O_3Ag_2$ , forms a black-brown precipitate which detonates when heated; the *ethyl-derivative*,  $C_{19}H_8(NO_2)_4O_3Et_2$ , obtained by heating the silver salt with ethyl iodide, melts at  $105^{\circ}$ , dissolves readily in benzene and alcohol, but is insoluble in water and alkaline carbonates. The *silver salt of tetrabromaurin*,  $C_{19}H_8Br_4O_3Ag_2$ , forms a dark-violet precipitate which when dry has a strongly metallic lustre; it is insoluble in water, ether, and benzene. The *ethyl-derivative*,  $C_{19}H_8Br_4O_3Et_2$ , is readily soluble in alcohol, ether, and benzene, insoluble in alkaline carbonates; it forms reddish microscopic crystals melting at  $110$ — $115^{\circ}$ . The *silver salt of tetrabromorosalic acid*,  $C_{20}H_{10}Br_4O_3Ag_2$ , is obtained as a dark-violet precipitate; the *ethyl-derivative*,  $C_{20}H_{10}Br_4O_3Et_2$ , melts at  $110$ — $115^{\circ}$ , is soluble in alcohol, benzene, and ether, but insoluble in water and alkaline carbonates.

A. K. M.

**Fluoresceïns from Maleic Acid.** By G. LUNGE and R. BURCKHARDT (*Ber.*, **17**, 1598—1600).—Maleic anhydride (1 mol.) and resorcinol (2 mols.) are heated together for two hours at  $150^{\circ}$ , the product poured into cold water, and then extracted with boiling water. The solution on cooling deposits a yellowish-red substance, which decomposes above  $240^{\circ}$  without melting. Its formation may be expressed thus:—



This fluoresceïn of maleic acid is sparingly soluble in water, more readily in alcohol and in other indifferent solvents. Its alcoholic solution is yellowish-red with greenish fluorescence; the addition of soda or ammonia produces a splendid magenta coloration, with strong green fluorescence. Lead acetate produces a reddish-brown precipitate,  $C_{16}H_8O_6Pb$ , 1 mol.  $H_2O$  being eliminated; barium acetate also yields a precipitate, but neither of these salts has been obtained in the crystalline state; silver nitrate produces decomposition; aluminium salts yield pink, and iron salts brownish-red compounds.

When maleic anhydride and  $\alpha$ -naphthol are heated together, no fluoresceïn appears to be formed, whilst in the presence of zinc chloride or sulphuric acid a substance is obtained soluble in water. Its alcoholic solution is bright yellow, with a deep yellow fluorescence; its ammoniacal solution is of a magenta colour, with yellowish-red fluorescence.  $\beta$ -Naphthol also yields a fluoresceïn, which gives a brown solution with alkalis, showing greenish-blue fluorescence, whilst from orcinol, a brown solution with moss-green fluorescence is obtained. Further experiments are being made.

A. K. M.

**Phenol Colouring Matters.** By C. KRAEMER (*Ber.*, **17**, 1875—1884).—After calling attention to the fact that the three compounds, nitrobenzene, Weselsky's reagent (nitrous nitric acid), and Liebermann's reagent (nitrosylsulphuric acid), give in reaction with phenols sometimes identical, sometimes different results, the author describes some new compounds related to the classes of bodies formed.



*Azoresorufin dimethyl ether*,  $[C_6H_4O_2N.C_6H_3(OMe)]_2O$ , obtained by heating paranitrotoluene with resorcinol and sulphuric acid, forms dark-red needles, soluble in alcohol to a purple liquid, having a vermilion fluorescence. Ortho- and meta-nitrotoluene appear to give no such reaction.

*Phenol-dyes*.—Exactly following Liebermann's direction for the preparation of his phenol-dye to which he ascribed the formula  $C_{18}H_{15}NO_3$  (this Journal, 1875, 167), the author finds that the product so obtained is a mixture of two substances, the one, A, soluble, the other, B, insoluble in ether. A, *soluble in ether*, has the formula  $C_{18}H_{15}NO_3$  ascribed to his compound by Liebermann. It forms a red amorphous mass, easily soluble in alcohol and ether, and is undoubtedly Liebermann's compound. Its constitution is probably  $OH.C_6H_4.N(OPh)_2$ . B, *insoluble in ether*, is a black amorphous mass, soluble in strong sulphuric acid to a green, and in alkalis to a brown liquid. When exposed to the atmosphere, it gradually becomes violet in colour, and this takes place immediately when it is treated with hypochlorites. In properties, it resembles the substance obtained by Lex (*Ber.*, 3, 457) by the action of potassium nitrite on an aqueous solution of phenol. It has the formula  $C_{18}H_{15}NO_4.H_2O$ , and is an oxidation-product of the soluble compound. Its constitution, therefore, is probably  $OH.C_6H_4.NO(OPh)_2 + H_2O$ .

*Orcinol-dyes*.—1. By the action of nitrosylsulphuric acid on orcinol, Liebermann obtained a green substance, to which he gave the formula  $C_{21}H_{18}N_2O_5$ , together with a second less nitrogenised compound. On repeating this experiment, the author has obtained two colouring matters, which are both soluble in alcohol, but can be separated by means of their sodium salts. The *sodium salt soluble in alcohol* yields a brown amorphous dye, having a green iridescence. In alkalis, it forms a red fluorescent solution. It has the formula  $C_{21}H_{21}NO_6$ , and the probable constitution  $C_6H_2Me(OH)_2.N(O.C_6H_3Me.OH)_2$ . The *sodium salt insoluble in alcohol* yields a very similar amorphous green mass, which dissolves in alkalis to a non-fluorescent violet solution. Its formula is  $C_{21}H_{21}NO_7$ , and therefore stands in the same relation to the substance just described, as the phenol-dye A does to B. Its constitution is probably  $C_6H_2Me(OH)_2.NO(O.C_6H_3Me.OH)_2$ .

2. With Weselsky's reagent, orcinol yielded a scarlet powder, having the formula  $C_{14}H_{11}NO_3$ , already ascribed to it by Weselsky. It is probably  $C_6H_2Me.O.N < \overset{O}{\underset{O}{\parallel}} > C_6H_4Me$ .

*Mononitroso-orcinol* was prepared by the action of amyl nitrite on the sodium compound of orcinol. It forms small dark red prisms which blacken at  $110^\circ$ . It is easily soluble in alcohol, ether, and acetone, sparingly so in water, and almost insoluble in chloroform. Its neutral alkali salts give with lead salts orange, with copper salts brown, and with mercuric salts yellow precipitates. When heated with orcinol and sulphuric acid, it yields Weselsky's dye,  $C_{14}H_{11}NO_3$ .

When nitrobenzene, orcinol, and sulphuric acid are heated together the same compound,  $C_{14}H_{11}NO_3$ , is produced, but only in exceedingly small quantity.

L. T. T.

**Action of Potassium Cyanide on Nitrated Benzaldehyde.**

By B. HOMOLKA (*Ber.*, **17**, 1902—1904).—The introduction of a nitro-group into benzaldehyde does not generally prevent it from forming condensation-products with acetone, aldehyde, acetic anhydride, &c.; but in some cases, as in the formation of benzoïn-derivatives, it does prevent such reaction. The action of potassium cyanide on *paranitrobenzaldehyde* yields *paranitrobenzoic acid*, together with a red resinous body not further investigated, whilst with *orthonitrobenzaldehyde*, *orthazoxybenzoic acid*, described by Griess (*this Jour.*, 1875, 460), is formed. This acid was converted into *orthohydrazobenzoic acid*, which crystallises in scales (m. p. 205°).

L. T. T.

**Benzeneazoketone.**

By V. v. RICHTER and H. MÜNZER (*Ber.*, **17**, 1926—1930).—When ethylic benzeneazoacetoacetate, prepared according to V. Meyer's directions (*Abstr.*, 1878, 396), is heated with an alcoholic or aqueous solution of caustic soda, *benzeneazoacetone*,  $\text{Ph.N}_2\text{CH}_2\text{COMe}$ , is formed. It crystallises in pale yellow needles or prisms which melt at 148—149°, and are easily soluble in alcohol, sparingly so in boiling water. The decomposition takes place entirely in the ketone direction, no benzeneazoacetic acid being formed. Benzeneazoacetone has a characteristic odour. Another method of preparation is to heat free benzeneazoacetoacetic acid to 170—180°, when carbonic anhydride is eliminated. Attempts to oxidise the ketone to benzeneazoacetic acid were unsuccessful.

*Ethylic paratolueneacetoacetate*, prepared in a similar manner, crystallises in yellow needles, which melt at 69—70°. When saponified with caustic soda, *paratolueneazoacetone*,  $\text{C}_6\text{H}_4\text{Me.N}_2\text{CH}_2\text{COMe}$ , is formed. This crystallises in yellow needles melting at 114—115°. It is also formed from the free acid by heat.

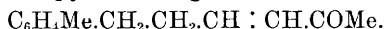
L. T. T.

**Action of Chromyl Chloride on Cymene.**

By V. v. RICHTER and G. SCHÜCHNER (*Ber.*, **17**, 1931—1935).—By the action of chromyl chloride on cymene, Étard obtained two aldehydes of the formula  $\text{C}_6\text{H}_4\text{Pr}^a\text{COH}$ ; isocumaldehyde melting at 81° and boiling at 220°, and terecumaldehyde, a liquid boiling at 219—220° (*Ann. Chim. Phys.* [5], **22**, 259). As Paternò and Scichilone (*Abstr.*, 1881, 423) could not obtain an aldehyde from cymene it appeared advisable to repeat the reaction.

The authors employed the pure paracymene obtained by heating camphor with phosphoric anhydride (cf. Armstrong and Miller, *this vol.*, p. 44). The oxidation was effected according to Étard's directions. Although the preparation was repeated many times, only a single aldehyde was obtained, and was found to be not a cumaldehyde, but the isomeric *paratolylpropaldehyde*,  $\text{C}_6\text{H}_4\text{Me.CH}_2\text{CH}_2\text{COH}$  [1:4]. It is a colourless strongly refractive oil, boils at 222—223°, has a peculiar peppermint-like odour, does not solidify at -15°, and at 13° has a sp. gr. 0.9941. It unites with hydrogen sodium sulphite to form a compound of the formula  $\text{C}_{10}\text{H}_{12}\text{O.HNaSO}_3$ , crystallising in white nacreous needles. It reduces ammoniacal silver solution and gives a violet coloration with a solution of magenta decolorised by

sulphurous acid. By oxidation with potassium permanganate, it yields terephthalic acid, and with nitric acid, it gives paratoluic acid together with small quantities of terephthalic acid and of a nitro-acid. The aldehyde unites with phenylhydrazine to form an oily compound. With acetone, in presence of potash, it yields an oil giving numbers on analysis approximating to the formula



Experiments are in progress to endeavour to oxidise the aldehyde to paratolylpropionic acid. Étard's results are probably due to his employment of the impure cymene obtained by the action of bromine on turpentine.

A. J. G.

**Amidoacetophenone and Allied Substances.** By P. KLINGEL (*Ber.*, 17, 1613—1614).—When a mixture of aniline, zinc chloride, and an excess of acetic anhydride, is boiled for several hours, the acetyl-derivative of paramidoacetophenone is produced, from which paramidoacetophenone,  $\text{COMe}.\text{C}_6\text{H}_4\text{NH}_2$ , may be obtained, having all the properties assigned to it by Drewsen (*Annalen*, 212, 163). Acetorthamidotoluene,  $\text{COMe}.\text{C}_6\text{H}_3\text{Me}.\text{NH}_2$ , may be obtained in the same way; it forms needles when crystallised quickly, and prisms when slowly crystallised; it melts at  $102^\circ$ . The platinum-chloride,  $(\text{C}_9\text{H}_{11}\text{NO})_2.\text{H}_2\text{PtCl}_6$ , forms slender, yellow, sparingly soluble needles. Acetoparamidotoluene is more difficult to prepare. The author is continuing the experiments.

A. K. M.

**Preparation of Vanillin.** By HAARMANN and REIMER (*Dingl. polyt. J.*, 253, 391).—When coniferin is oxidised with aqueous chromic acid, it is converted into glucovanillin. For this purpose a solution of 10 parts coniferin in 200 parts water, is treated at the ordinary temperature with a solution of 8 parts chromic acid dissolved in a small quantity of water, and the mixture allowed to stand for several days. Barium carbonate is then added to precipitate the chromium. The solution is evaporated to a small bulk, treated with alcohol and filtered. The filtrate, on evaporation, yields crystals of glucovanillin, melting at  $170^\circ$ . Concentrated sulphuric acid dissolves coniferin, forming a deep violet solution, whilst with glucovanillin it gives a pale yellow solution. On treating glucovanillin with emulsin in aqueous solution, or on boiling it with dilute mineral acids, it is resolved into glucose and vanillin. The latter may be extracted from the solution by ether.

D. B.

**Cinnamaldehyde.** By T. ZINCKE and D. v. HAGEN (*Ber.*, 17, 1814—1817).—When an alkaline aqueous solution of cinnamaldehyde is treated with potassium cyanide, a yellow amorphous product is formed, which is soluble in alcohol, acetic acid, &c., and gives numbers on analysis very close to those required by cinnamaldehyde. The authors have not further investigated this substance.

*Cinnamaldehyde dibromide*,  $\text{CHPhBr}.\text{CHBr}.\text{COH}$ , is obtained by the direct addition of bromine to the aldehyde dissolved in ether, chloroform, or carbon bisulphide. It crystallises in small needles, which melt at  $100^\circ$ , with evolution of hydrobromic acid, and have a

very pungent odour. It is very unstable, deliquesces on keeping, and gives off hydrobromic acid. When boiled with alcohol or acetic acid it gives off hydrobromic acid, and forms *monobromocinnamaldehyde*,  $\text{CPhBr} : \text{CH} \cdot \text{COH}$ ; this is, however, best prepared by the action of potassic acetate on the dibromide. Monobromocinnamaldehyde crystallises in plates or monoclinic prisms, soluble in alcohol and ether. It melts at  $72-73^\circ$ , and is very stable. Alcoholic potash, ammonia, and aniline, react with it at high temperatures, but no satisfactory results were obtained. It does not combine with bromine, but with phenylhydrazine it yields the compound,



which forms glistening yellow scales melting at  $129-130^\circ$ . When boiled with an acetic solution of chromic acid, the monobrominated derivative is oxidised to  $\alpha$ -bromocinnamic acid, thus proving the correctness of the above formula. Monobromocinnamaldehyde when treated at  $10^\circ$  with nitric acid of 1.5 sp. gr., yields two *mononitro-derivatives*. The  $\alpha$ -compound (which is the less soluble in alcohol) forms yellowish needles melting at  $136^\circ$ , and yields a ruby-coloured compound with phenylhydrazine; this melts at  $154^\circ$ , and by the action of reducing agents is converted into an easily soluble base, which is now under investigation. The  $\beta$ -compound forms yellow needles melting at  $96-97^\circ$ , and yields a hydrazine-compound crystallising in large golden-yellow scales, melting with decomposition at  $134^\circ$ . This  $\beta$ -compound also yields a base on reduction. L. T. T.

**Derivatives of Cinnamaldehyde.** By G. PEINE (*Ber.*, 17, 2109—2118).—*Hydrocinnamide* ( $\text{C}_{27}\text{H}_{24}\text{N}_2 = \text{N}_2(\text{CH} \cdot \text{CH} : \text{CHPh})_3$ ).—Laurent obtained a compound to which he assigned this name and formula by the action of ammonia on oil of cinnamon. The author finds the first product of the reaction to have a more complex constitution; but by treatment in alcoholic solution with concentrated hydrochloric acid, hydrocinnamene hydrochloride is obtained, although the yield is very small owing to the formation of resinous bye-products. By shaking together for some weeks aqueous ammonia and an ethereal solution of cinnamaldehyde, a good yield of hydrocinnamide is obtained. It crystallises in white needles, melts at  $106^\circ$ , and is not decomposed by heating with concentrated hydrochloric acid for some hours at  $250^\circ$ . The hydrochloride,  $\text{C}_{27}\text{H}_{24}\text{N}_2 \cdot \text{HCl} + 3\text{H}_2\text{O}$ , crystallises in colourless tables, melts at  $220-221^\circ$ , is soluble in alcohol and chloroform, insoluble in water, ether, benzene, and light petroleum. The platinochloride has the formula  $(\text{C}_{27}\text{H}_{24}\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$ . Experiments to convert hydrocinnamide into bodies resembling amarine and lophine were not successful.

*Phenyl- $\alpha$ -hydroxycrotonitrile*,  $\text{CHPh} : \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{CN}$ , is obtained by mixing an ethereal solution of cinnamaldehyde with a slight excess of potassium cyanide, and adding concentrated hydrochloric acid, drop by drop, until no more hydrocyanic acid is evolved. It forms a crystalline mass, melts at  $75^\circ$ , is readily soluble in alcohol, ether, benzene, and chloroform, insoluble in light petroleum.

*Phenyl- $\alpha$ -hydroxycrotonic acid*,  $\text{CHPh} : \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{COOH}$ , is pre-

pared by boiling the nitrile for several hours with dilute hydrochloric acid. It crystallises in long, flat needles, and melts at 115–116°. It has been previously obtained by Matsmoto (this Journal, 1876, i, 80). The methyl salt,  $C_9H_8(OH).COOMe$ , forms a clear yellow liquid of ethereal odour, and boils at 290°. The ethyl salt,  $C_9H_8(OH).COOEt$ , boils at 295°.

*Phenyl- $\alpha$ -anilidocrotononitrile*,  $CHPh : CH(CHPh).CN$ , obtained by boiling alcoholic solutions of aniline and phenyl- $\alpha$ -hydroxycrotononitrile, is crystalline, melts at 130°, is insoluble in water and light petroleum, readily soluble in alcohol, ether, benzene, and chloroform. By dissolving it in concentrated sulphuric acid, and pouring the solution into water, it is converted into *phenyl- $\alpha$ -anilidocrotonamide*,  $CHPh : CH.CH(NHPh).CONH_2$ . This crystallises in thin plates, melts at 171°, is readily soluble in alcohol and chloroform, sparingly soluble in hot water.

*Phenyl- $\alpha$ -anilidocrotonic acid*,  $CHPh : CH.CH(NHPh).COOH$ , prepared by the action of hydrochloric acid on the amide, crystallises in microscopic needles, melts at 154°, is readily soluble in alcohol, ether, and chloroform, somewhat soluble in benzene, insoluble in water and light petroleum. Possessing both acid and basic properties, it dissolves in solutions of acids and bases. With a solution of the ammonium salt, barium, zinc, lead, and silver salts give white crystalline precipitates; copper salts give a green precipitate which can be obtained crystallised in needles of the formula  $(C_6H_{14}NO_2)_2Cu$ .

Cinnamaldehyde can be synthesised by heating a mixture of benzaldehyde (10 parts), acetaldehyde (15 parts), water (900 parts), and aqueous soda of 10 per cent. (10 parts), with frequent shaking for 8–10 days at a temperature of about 30°.

*Salts of Cinnamaldehyde-anilide*.—The hydrochloride forms yellow needles and melts at 149°. The sulphate,  $(C_{15}H_{13}N)_2H_2SO_4$ , crystallises in yellow needles and melts at 157°; the nitrate also crystallises in yellow needles. The platinumchloride,  $(C_{15}H_{13}N)_2H_2PtCl_6$ , crystallises well.

A. J. G.

**Condensations with Orthonitrocinnamaldehyde.** By A. EINHORN (*Ber.*, 17, 2026–2028).—Baeyer and Drewson have shown (this vol., p. 58) that orthonitrobenzaldehyde and acetaldehyde react to form a loose compound of orthonitrophenyllactic aldehyde with 1 mol. acetaldehyde; and this, when boiled with acetic anhydride is converted into orthonitrocinnamaldehyde. The author now shows that orthonitrocinnamaldehyde can further react with acetaldehyde to form a condensation-product. Nitrocinnamaldehyde is mixed with 7–8 times the amount of acetaldehyde, and dilute soda added from time to time until a permanent alkaline reaction is obtained. At first the reaction is moderated by cooling the containing vessel with ice-water, later on the temperature is allowed to rise. The product is separated by precipitation with water and purified by treatment with animal charcoal and recrystallisation from alcohol. It then forms sulphur-yellow crystals and melts at 153°. It combines readily with bromine and shows all the properties of an aldehyde. Its analysis agrees with the formula  $C_{11}H_9NO_3$ , and it is probably

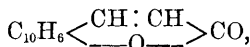
*orthonitrocinnamylacetaldehyde*. Its further investigation is in progress. A. J. G.

**Some New Coumarins.** II. By H. v. PECHMANN and W. WELSH (*Ber.*, **17**, 1646—1652).—This is a continuation of Pechmann's work on the production of coumarins, by the action of sulphuric acid and a phenol on malic acid (this vol., p. 1173). It is found that the different phenols behave very differently, although phloroglucol is the only one experimented with which did not yield a coumarin-like compound; thus, whilst resorcinol, orcinol, and pyrogallol give an abundant yield of the respective coumarins, only small quantities are obtained from phenol, cresol, thymol, quinol, and naphthol.

*Orthomethylparapropylcoumarin*,  $C_6H_2MePr<\text{CH:CH}>CO$ , obtained from malic acid and thymol, crystallises from water or very dilute alcohol in slender white needles; it has an odour resembling that of thymol and coumarin. It melts at  $53^\circ$ , distils between  $220^\circ$  and  $230^\circ$ , is very sparingly soluble in water, readily in alcohol, ether, glacial acetic acid, benzene, and chloroform. In its behaviour to alkalis it resembles ordinary coumarin.

*Metahydroxycoumarin*,  $OH.C_6H_3<\text{CH:CH}>CO$ , prepared from malic acid and quinol, is isomeric with umbelliferone. It melts at  $248-250^\circ$ , dissolves sparingly in water, readily in alcohol and glacial acetic acid; it yields colourless solutions with concentrated sulphuric acid and with alkalis, and gives no reaction with ferric chloride. When boiled with acetic anhydride, it forms an *acetyl-derivative* which crystallises in splendid needles melting at  $147^\circ$ , is insoluble in water, but readily soluble in alcohol, ether, benzene, and chloroform.

*Homo-umbelliferone*,  $OH.C_6H_2Me<\text{CH:CH}>CO$ , from malic acid and orcinol, melts at  $248^\circ$ , dissolves in alcohol, glacial acetic acid, and acetone, and is insoluble in water, benzene, and chloroform. In its physical and chemical properties it bears a strong resemblance to umbelliferone. It forms blue fluorescent solutions with alkalis which become colourless on heating; its solution in concentrated sulphuric acid also exhibits blue fluorescence. Ferric chloride shows no reaction. By fusion with potash, it is converted into acetic acid, and orcyaldehyde,  $C_6H_5O_3$  (*Ber.*, **12**, 1001); this melts at  $179^\circ$ , is soluble in alcohol, ether, and chloroform, gives a reddish-brown reaction with ferric chloride, and yields a crystalline compound with phenylhydrazine. The *acetyl-derivative* of homo-umbelliferone melts at  $126-127^\circ$ , and is identical with Tiemann and Helkenberg's homacetoxycoumarin (*Ber.*, **12**, 1002). The compound,



obtained from  $\beta$ -naphthol and malic acid, is different from Kauffmann's  $\beta$ -naphthacoumarin (*Abstr.*, 1882, 1068). It crystallises from dilute alcohol in yellowish needles, melts at  $141^\circ$ , is insoluble in water, sparingly soluble in ether, readily in alcohol, acetic acid,

benzene, and chloroform.  $\alpha$ -Naphthol yields mere traces of a crystalline condensation-product. Attempts to prepare æsculetin from malic acid and phloroglucol yielded no coumarin. The dihydroxy-coumarin obtained by the condensation of phloroglucol with ethyl acetoacetate, does not bear the slightest resemblance to æsculetin. From these results, it seems probable that æsculetin bears no relation to phloroglucol, and the authors intend to try to produce it from Barth and Schreder's hydroxyquinol (Abstr., 1883, 987).

A. K. M.

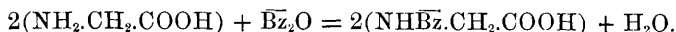
**Bromoxylic Acid and Hydroxyxylic Acid.** By E. GUNTER (*Ber.*, 17, 1608—1609).—Süssenguth's monobromopseudocumic acid is a bromoxylic acid, identical with that obtained on brominating xylic acid dissolved in glacial acetic acid. When treated with sodium-amalgam, it yields xylic acid (m. p. 126°), and on heating this with hydrochloric acid at 220°, metaxylene is obtained. By fusing the brominated acid with potash, three hydroxy-acids are obtained. The acid formed in largest quantity melts at 170·5°, yields no blue coloration with ferric chloride, is scarcely volatile in steam, and is not decomposed by hydrochloric acid at 200—210°. Assuming that no molecular change occurs during its formation, its constitution must be  $C_6H_2Me_2(OH).COOH$  [OH : Me : Me : COOH = 1 : 2 : 4 : 5]. The second acid melts at 144°, gives a blue colour reaction with ferric chloride, is readily volatile in steam, and is completely decomposed on heating it with hydrochloric acid at 200—210°, yielding carbonic anhydride and *paraxyleneol*; this shows that it has the constitution  $C_6H_2Me_2(OH).COOH$  [Me : OH : COOH : Me = 1 : 2 : 3 : 4]. The third hydroxy-acid melts at 153°, is not coloured blue by ferric chloride, and yields *paraxyleneol* when heated with hydrochloric acid at 200—210°; its constitution is therefore



From these results, it would appear that either a molecular change takes place by the action of potash on the bromoxylic acid, or that the latter is mixed with isomeric acids, which, however, is not probable. On brominating paraxylic acid, a monobromo-derivative is obtained, crystallising in slender white needles melting at 189°; it dissolves readily in alcohol, sparingly in water. The *barium salt* is moderately soluble, and crystallises in dense aggregates of needles; the *calcium salt* forms groups of colourless prisms easily soluble in hot water; the *cadmium salt* forms readily soluble flat white prisms; the *potassium salt* crystallises in small needles readily soluble in water, and the *copper salt* in small blue rhombic plates.

A. K. M.

**Synthesis of Hippuric Acid and Hippuric Ethers.** By T. CURTIUS (*Ber.*, 17, 1662—1663).—A good yield of hippuric acid is obtained by the action of benzoic anhydride on glycocoll:



Finely powdered dry glycocine is gradually added to an excess of hot benzoic anhydride, and the whole heated in an oil-bath until a red mass is obtained; this is dissolved in water, neutralised with alkali,

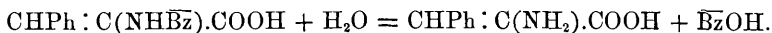
acidulated, and allowed to remain for some days. The precipitate is boiled with water, using animal charcoal, and the filtrate is concentrated and allowed to crystallise. The product contains some benzoic acid, which may be removed by treatment with light petroleum. In order to prepare ethyl hippurate, a mixture of benzoic anhydride and glycooll ether in calculated quantities is digested at about  $100^{\circ}$  and the product crystallised from boiling water; it forms white needles which melt at  $60^{\circ}$ .  
A. K. M.

**Derivatives of Phenylcinnamic Acid.** By A. G. CABELLA (*Gazzetta*, **14**, 114—116).—Phenylcinnamic acid was prepared by Ogliastro (Abstr., 1879, 640), and its silver, lead, barium, and ethyl salts examined and described. The author has prepared *methylic phenylcinnamate*,  $\text{CHPh} : \text{CPh}.\text{COOMe}$ , by passing dry hydrochloric acid gas into a solution of the acid in methyl alcohol. It crystallises from dilute alcohol in long needles which melt at  $77\text{--}78^{\circ}$ . Bromine does not combine with it when the two are dissolved in chloroform and allowed to remain at the ordinary temperature, but if the mixture is heated in a water-bath, in a flask furnished with a reflux condenser, an action takes place, and the dibrominated compound,  $\text{CHBrPh}.\text{CBrPh}.\text{COOMe}$ , is obtained. This crystallises in transparent plates which melt at  $105\text{--}108^{\circ}$ . The bromine in it could not be determined by Carius' method, as it was not completely oxidised by the nitric acid.  
C. E. G.

**Derivatives of Benzoylimidocinnamic Acid.** By J. PLÖCHL (*Ber.*, **17**, 1616—1624).—The author refers to a previous paper (this vol., p. 604) in which he described the formation of benzoylimidocinnamic acid by the condensation of hippuric acid with benzaldehyde, and also its decomposition by acids or alkalis into benzoic acid, ammonia, and phenylglycidic acid. When benzoylimidocinnamic acid is heated in a sealed tube with concentrated aqueous ammonia, the *lactimide of benzoyldiamidohydrocinnamic acid*,  $\text{CHPh} \left\langle \begin{array}{c} \text{CH}(\text{NH}\text{Bz}) \\ \text{---NH---} \end{array} \right\rangle \text{CO}$ , is obtained, crystallising in lustrous needles or prisms. It melts at  $187^{\circ}$ , is insoluble in water, dilute acids, or alkalis, sparingly soluble in ether, but more readily in hot alcohol or acetic acid; it is very stable, but may be decomposed by hot mineral acids or caustic alkalis. The ammoniacal mother-liquors from the lactimide contain benzamide and an acid,  $\text{C}_{16}\text{H}_{13}\text{O}_3\text{N}$ , isomeric with benzoylimidocinnamic acid. The acid  $\text{C}_{16}\text{H}_{13}\text{O}_3\text{N}$  is separated from its ammonium salt by adding a mineral acid, and is purified by crystallisation from dilute acetic acid; it melts at  $131^{\circ}$ , dissolves very readily in ether and alcohol, is also soluble in hot water and crystallises in needles or prisms. It is identical with  *$\alpha$ -benzoylamidocinnamic acid*, obtained as given below, and its formation from benzoylimido-cinnamic acid is explained by a simple molecular change similar to that of hydrobenzamide into amarine (Abstr., 1882, 329).  *$\alpha$ -Benzoylamidocinnamic acid*,  $\text{CHPh} : \text{C}(\text{NH}\text{Bz}).\text{COOH}$ , is prepared by heating the lactimide of benzoyldiamidohydrocinnamic acid in acetic acid solution with a quantity of dilute hydrochloric acid rather more than sufficient to



remove 1 mol.  $\text{NH}_3$ ; as the solution cools, the acid crystallises out in nodular groups of prisms.  $\alpha$ -Amidocinnamic acid,  $\text{CHPh}:\text{C}(\text{NH}_2).\text{COOH}$ , is prepared by heating benzoylamidocinnamic acid, or the lactimide of the benzoilyldiamido-acid, with 20 per cent. hydrochloric acid at  $120^\circ$ . The acid liquid is separated from the benzoic acid produced, evaporated to dryness, the residue dissolved in a little water and the amido-acid separated by the addition of sodium carbonate or acetate. It forms white scales of silvery lustre, and in its physical properties is scarcely to be distinguished from phenylalanine. When heated in a capillary tube, it is gradually decomposed between  $240$ – $250^\circ$ , whilst phenylalanine melts above  $260^\circ$  with vigorous evolution of carbonic anhydride. Its copper salt,  $(\text{C}_9\text{H}_9\text{NO}_2)_2\text{Cu} \cdot 2\text{H}_2\text{O}$ , also agrees in its properties with that of phenylalanine, and in the amount of water of crystallisation. The hydrochloride of amidocinnamic acid has the composition  $(\text{C}_9\text{H}_9\text{NO}_2)_2\text{HCl}$ , and crystallises in flat needles, sparingly soluble in cold water and alcohol, whilst phenylalanine yields a normal hydrochloride, readily soluble in water but very sparingly in concentrated hydrochloric acid. When rapidly heated,  $\alpha$ -amidocinnamic acid yields styrolamine and the lactide of the acid, phenylalanine yielding phenylethylamine and a lactimide. With nitrous acid, a sparingly soluble oily hydroxy-acid, probably  $\alpha$ -hydroxycinnamic acid, is obtained. The formation of the amidocinnamic acid is expressed thus:

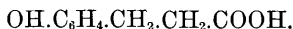


But besides this reaction, another takes place resulting in the formation of phenylacetic acid. Reducing agents convert amidocinnamic acid into phenylalanine, identical with that obtained by Erlenmeyer and Lipp (*Annalen*, **219**, 200).

A. K. M.

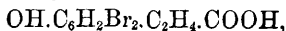
**Hydroparacoumaric Acid.** By G. C. STÖHR (*Annalen*, **225**, 57–94).—Considerable interest is attached to hydroparacoumaric acid, chemically, from its connection with the cinnamic acid group, and physiologically, as a product of the decomposition of tyrosine from the albumin in the intestines; as such, it has been found in patients suffering from peritonitis, and in normal human urine. The ethyl salt of this acid is also probably present in the rhubarb.

The acid is best prepared by converting ethyl paranitrocinnamate by hydrogenation into paramidohydrocinnamic acid, which by means of the diazo-compound is then transformed into the corresponding hydroxyl-compound, or *hydroparacoumaric acid*,



It crystallises from its solutions in ether in pale-golden prisms of the monoclinic system; it melts at  $128^\circ$ . It gives a characteristic blue coloration with ferric chloride, the phenol reaction with nitrous acid, and a white precipitate with mercuric nitrate. It does not reduce Fehling's solution. The salts of this acid have been described by Hlasiwetz and Baumann.

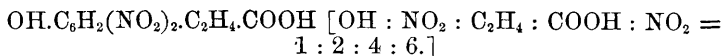
With bromine, the acid yields a *dibromo-derivative*,



which crystallises in needles melting at  $107^{\circ}$ ; its *ammonium* salt forms colourless needles; its silver, copper, and lead salts are amorphous precipitates.

*Dinitrohydroparacoumaric acid*,  $\text{OH.C}_6\text{H}_2(\text{NO}_2)_2.\text{CH}_2.\text{COOH}$ , obtained by the action of concentrated nitric acid on hydroparacoumaric acid, forms flat prismatic crystals of the rhombic system, melting at  $137.5^{\circ}$ , soluble in alcohol and acetic acid. This acid forms two series of salts, the one strongly acid, decomposing carbonates, the other neutral. Of the former, the *ammonium* salt crystallises in reddish-golden needles, the *silver* salt in grouped needles, the *calcium* salt in golden prisms; the *iron* and *copper* salts are amorphous precipitates; of the latter the *ammonium* salt crystallises in golden needles, and the *silver* salt in dark-red needles. The hydrogen ethereal salts are best obtained by saturating alcoholic solutions of the acid with hydrochloric acid, and the neutral ethereal salts by the action of the alcoholic iodides on the silver ethereal salts. Of the former, the *methyl* salt crystallises in long, colourless needles melting at  $87^{\circ}$ , the *ethyl* salt in citron, six-sided tables; both decompose carbonates readily. Of the latter, the *dimethyl* salt forms colourless prismatic needles, melting at  $53^{\circ}$ ; the *methyl ethyl* salt,  $\text{MeO.C}_6\text{H}_2(\text{NO}_2)_2.\text{C}_2\text{H}_4.\text{COOEt}$ , colourless glistening needles melting at  $71^{\circ}$ ; the *ethyl methyl*,  $\text{EtO.C}_6\text{H}_2(\text{NO}_2)_2.\text{C}_2\text{H}_4.\text{COOMe}$ , colourless needles melting at  $36^{\circ}$ , and the *diethyl* salt, glistening needles melting at  $49^{\circ}$ .

*Dinitromethylhydroparacoumaric acid*,  $\text{MeO.C}_6\text{H}_2(\text{NO}_2)_2.\text{C}_2\text{H}_4.\text{COOH}$ , obtained by the decomposition of either the methyl ethyl or dimethyl salt by heating it with sulphuric acid, crystallises in aggregated flat prisms melting at  $124^{\circ}$ , readily soluble in alcohol; the corresponding *ethyl* compound in long colourless needles melting at  $126^{\circ}$ . In order to determine the relative position of the two nitro-groups in dinitrohydroparacoumaric acid, its methyl salt was subjected to oxidation by chromic mixture; dinitroanisic acid was obtained, convertible into chrysanic and dinitroparoxybenzoic acids and  $\beta$ -dinitrophenol. These results show that the two nitro-groups are in the ortho-position to the hydroxyl, and in the meta-position to the side-chain: thus to dinitrohydroparacinnamic acid must be ascribed the formula



*Dinitroparamidohydrocinnamic acid*,  $\text{NH}_2.\text{C}_6\text{H}_2(\text{NO}_2)_2.\text{C}_2\text{H}_4.\text{COOH}$ , obtained from the above-mentioned methyl salt by heating it with ammonia, crystallises in dark-golden needles with a green reflection; it melts at  $190^{\circ}$ , is sparingly soluble in cold, but moderately in hot water and in alcohol. Its metallic salts crystallise in golden needles, its *methyl* salt in brilliant reddish leaflets melting at  $102^{\circ}$ , its *ethyl* salt in golden-yellow leaflets melting at  $95^{\circ}$ . The acid and its ethereal salts are readily converted by heating with alkalis into dinitrohydroparacoumaric acid.

*Mononitrohydroparacoumaric acid*,  $\text{HO.C}_6\text{H}_3(\text{NO}_2).\text{C}_2\text{H}_4.\text{COOH}$ , obtained from hydroparacoumaric acid by treatment with nitric acid, crystallises in tufts of needles melting at  $90.5^{\circ}$ ; its *methyl* salt crystallises in golden needles melting at  $64^{\circ}$ , and its *ethyl* salt in concentric

cally-grouped golden needles melting at 30°. As the acid does not yield hydroxyhydrocarbostyryl on reduction, the nitro-group is in the ortho-position to the hydroxyl-group, and in the meta to the side-chain. The formula

$\text{OH.C}_6\text{H}_3(\text{NO}_2).\text{C}_2\text{H}_4.\text{COOH}$  [ $\text{OH} : \text{NO}_2 : \text{C}_2\text{H}_4.\text{COOH} = 1 : 2 : 4$ ],  
therefore represents its constitution. V. H. V.

**Etherification of the Three Isomeric Nitrophenyl- $\beta$ -lactic Acids.** By A. EINHORN and G. PRAUSNITZ (*Ber.*, **17**, 1659—1662).—According to Basler (*Ber.*, **16**, 3007), paranitrophenyl- $\beta$ -lactic acid may be converted into the corresponding  $\beta$ -lactone by heating it with an alcoholic solution of zinc chloride. The authors have repeated the experiment, but cannot confirm Basler's results; not a trace of lactone could be detected in the product, which consisted of the ethyl-derivative of the acid, or, when methyl alcohol was employed, of the methyl-derivative. Ortho- and meta-nitrophenyl- $\beta$ -lactic acids yield the same results. Orthonitrophenyl- $\beta$ -lactic acid was heated with methyl alcohol and zinc chloride for 2—3 hours at 100°, and also 120°, and the product when cold poured into water. The methyl orthonitrophenyl- $\beta$ -lactate,  $\text{C}_{10}\text{H}_{11}\text{NO}_5$ , obtained melts, after purification, at 50—51°, and is identical with the product of the action of hydrochloric acid on orthonitrophenyl- $\beta$ -lactic acid and methyl alcohol. When either of the three nitrophenyl- $\beta$ -lactic acids is heated on a water-bath with aqueous zinc chloride, no action takes place, the original substance being recovered unchanged. Metanitrophenyl- $\beta$ -lactic acid was treated as above, ethyl alcohol being employed; no carbonic anhydride was evolved on heating at 120°, which should have been the case had a lactone been present: the product,  $\text{C}_{11}\text{H}_{13}\text{NO}_5$ , melts at 56°, and is identical with the ethyl-derivative obtained by boiling silver metanitrophenyl- $\beta$ -lactate with ethyl iodide. The same experiment was made with paranitrophenyl- $\beta$ -lactic acid, using methyl and ethyl alcohols, and here again no carbonic anhydride could be detected. The methyl ether melts at 73—74° (72—74° Basler), and the ethyl ether,  $\text{C}_{11}\text{H}_{13}\text{NO}_5$ , at 45—46°, as given by Basler. A. K. M.

**$\beta$ -Lactone of Isopropylnitrophenyllactic Acid.** By A. EINHORN and W. HESS (*Ber.*, **17**, 2015—2026).—By the nitration of cumenylacrylic acid in the cold, there is obtained orthonitrocumenylacrylic acid, and a small quantity (10—12 per cent.) of paranitrocinnamic acid. The formation of the latter is interesting, there being no analogous case of so moderately energetic a reagent as cold nitric acid splitting off an alkyl-group from a substituted benzene, and replacing it by a negative group. The acids are separated by repeated crystallisation from hot alcohol, in which paranitrocinnamic acid is but sparingly soluble.

*Orthonitrocumenylacrylic acid*,  $\text{C}_6\text{H}_3\text{Pr}^2(\text{NO}_2).\text{CH} : \text{CH}.\text{COOH} = [4 : 2 : 1]$ , when perfectly pure, crystallises in long, pale wine-yellow needles, and melts at 156—157° (as ordinarily obtained in a nearly pure state, it forms hard prismatic crystals, and melts at 152—153°). It is readily soluble in alcohol, ether, benzene, chloroform, and glacial

acetic acid; sparingly soluble in hot water, and insoluble in light petroleum. It gives a brown coloration when heated with concentrated hydrochloric acid. The barium salt crystallises in needles; the silver, lead, zinc, and copper salts are sparingly soluble precipitates; the methyl salt forms tufts of thin needles. As the nitrocumaldehyde obtained on oxidation is not the known metaldehyde (metacuminol, melting at  $54^{\circ}$ ), the nitro-group must be in the ortho-position.

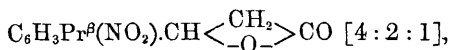
*Orthonitrocumaldehyde*,  $C_6H_3Pr^{\beta}(NO_2).COH$  [4 : 2 : 1], is prepared by oxidising the nitrocumenylacrylic acid with potassium permanganate, the well-cooled liquid being shaken with benzene throughout the oxidation. On evaporating the benzene, the aldehyde is left as an oil, and is purified by distillation with steam, conversion into the bisulphite-compound, &c. It then forms an oil, showing but little tendency to crystallise, even after standing for some days over sulphuric acid at the summer temperature. It reduces ammoniacal silver solution, and yields a compound with hydrogen sodium sulphite, crystallising in needles. When treated with acetone and soda, it yields a blue colouring matter, which, from its properties, is undoubtedly di-isopropyl indigo. This reaction confirms the presence of a nitro-group in the ortho-position.

*Para-isopropylorthonitrophenyl- $\beta$ -bromopropionic acid*,



is prepared by adding excess of glacial acetic acid, saturated at  $0^{\circ}$  with hydrobromic acid, to finely-powdered nitrocumenylacrylic acid. It crystallises in nearly colourless silky prisms, melts with decomposition at  $127^{\circ}$ , is readily soluble in alcohol, ether, benzene, chloroform, and glacial acetic acid, soluble in hot water, sparingly soluble in carbon bisulphide. On long boiling with water, it suffers decomposition, the liquid acquiring a green colour, and having an odour of nitroisopropylvinyl, and containing small quantities of nitrocumenylacrylic acid. Alkalis in the cold, and sulphuric acid on heating, remove the elements of hydrobromic acid, and regenerate nitrocumenylacrylic acid. From its chemical behaviour, and from analogy with the formation of the  $\beta$ -brominated acids by the action of hydrobromic acid on cinnamic and orthonitrocinnamic acids, there can be little doubt that the bromine-atom occupies the  $\beta$ -position.

*$\beta$ -Lactone of isopropylnitrophenyllactic acid*,

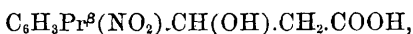


is best prepared by adding soda in very slight excess to the  $\beta$ -brominated acid, and allowing the solution to stand for 12 hours. In addition to the lactone, small quantities of nitrocumenylacrylic acid and isopropylnitrophenyllactic acid are formed. It crystallises in hard colourless crystals, melts at  $73^{\circ}$ , and on further heating is decomposed, leaving a blue residue that exhibits the indigo spectrum. It is readily soluble in alcohol, ether, benzene, glacial acetic acid, chloroform, and carbon bisulphide, sparingly in light petroleum. On boiling it with water, the chief products are carbonic anhydride and

isopropylnitrostyrene. Concentrated sulphuric acid dissolves it to a yellow solution, becoming green on heating; the addition of water precipitates a green colouring matter in flocks; this is soluble in chloroform. Hydrobromic acid reconverts the lactone into the brominated acid. By the action of alkalis, or their carbonates, or chalk, it is converted into the corresponding propylnitrophenyllactate.

*Isopropylnitrophenyllactamide*,  $C_6H_3Pr^{\beta}(NO_2).CH(OH).CH_2.CONH_2$  [4:2:1], prepared by the action of ammonia on the lactone or on the brominated acid, crystallises in stellate groups of pale yellowish-green prisms, melts at  $150^{\circ}$ , is readily soluble in hot water, benzene, chloroform, and glacial acetic acid, insoluble in ether and carbon bisulphide.

*Para-isopropylorthonitrophenyllactic acid*,



is best prepared by boiling the brominated acid with soda, separating the isopropylnitrostyrene formed simultaneously, by distillation with steam, and finally decomposing the sodium salt with an acid. (There appears to be no formation of nitrocumenylacrylic acid or di-isopropyl-indigo in this reaction, which thus differs from that with the lower homologues of the orthonitrocinnamic series.) It crystallises in silvery pale-yellow laminae, melts at  $119-120^{\circ}$ , is readily soluble in alcohol, ether, benzene, chloroform, glacial acetic acid, acetone, and hot water, sparingly soluble in carbon bisulphide, nearly insoluble in light petroleum. The sodium salt is crystalline; the calcium salt forms transparent prisms; the barium salt nodular groups of very slender needles; the cadmium salt forms roundish tables; the silver salt is obtained as a white precipitate, blackening on exposure to light; the copper, lead, and zinc salts are sparingly soluble precipitates. Hydrobromic acid reconverts the lactic acid into the brominated acid. Sulphuric acid removes the elements of water, nitrocumenylacrylic acid being formed.

*Isopropylnitrostyrene*,  $C_6H_3Pr^{\beta}(NO_2).CH:CH_2$  [4:2:1], prepared as mentioned above, is an oil of agreeable aromatic odour; it could not be solidified in a freezing mixture. It is very unstable, soon suffering spontaneous decomposition on standing. A. J. G.

**Caffeic Acid in Hemlock.** By A. W. HOFMANN (*Ber.*, 17, 1922—1923).—From the great similarity between conhydrine and tropine, the author believed that the former compound, like the latter, exists in plants in combination with an acid. He has now isolated caffeic acid from the alkaline residues left after driving over conine and conhydrine in the process of their extraction from hemlock. The alkaline residue was acidified and extracted with ether, and the residue then further purified. L. T. T.

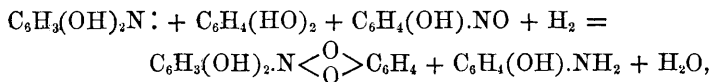
**Preparation of Phenolsulphuric Acid from Urine.** By L. BRIEGER (*Zeit. Physiol. Chem.*, 8 [4], 311—312).—The author's method may in some cases be advantageous, although Baumann's is the most accurate for quantitative determinations.

Fresh urine is treated with neutral acetate of lead as long as anything is precipitated, the precipitate filtered off, and the filtrate treated in the same way with basic lead acetate. From this filtrate the excess of lead is removed by sulphuretted hydrogen, the filtrate is evaporated to a thick syrup, and kept for some time in a vacuum. The potassium phenolsulphate which crystallises out in plates is purified by recrystallisation from hot absolute alcohol. A small quantity is retained by the basic lead acetate precipitate. J. P. L.

**Amidophenolsulphonic Acids and their Relationship to Liebermann's Colouring Matters.** By H. BRUNNER and C. KRAEMER (*Ber.*, **17**, 1867—1872).—When prepared by Brunner's reaction from resorcinol and nitrobenzene, azoresorufin, as already mentioned (p. 1333), is always accompanied by paramidophenolsulphonic acid. The latter is not formed when nitrobenzene alone is heated with sulphuric acid, so that its origin is evidently closely connected with the formation of azoresorufin. Taking into account the formation of azoresorufin from nitrosoresorcinol, the authors believe that during the progress of the above reaction an intramolecular rearrangement takes place in the nitrobenzene, somewhat according to the following equation:—



This dyad radicle  $\text{C}_6\text{H}_3(\text{OH})_2\text{N}:$  would at the moment of its formation react with a molecule of resorcinol and one of nitrosoresorcinol to form azoresorufin and paramidophenol—



the latter being converted into paramidophenolsulphonic acid and the former into azoresorufin by the excess of sulphuric acid. Sulphurous anhydride is always evolved during the reaction, and thus the nascent hydrogen required is accounted for.

The authors have also studied the action of the isomeric nitrophenols and of the homologues of nitrobenzene when heated with resorcinol and concentrated sulphuric acid. Paranitrotoluene and resorcinol yield a dimethyl ether of azoresorufin together with paramidophenolsulphonic acid, and not amidocresolsulphonic acid as might be expected. Of the three isomeric nitrophenols, the para-derivative alone yields a colouring matter analogous to resorufin, but all three yield amidophenolsulphonic acids. Only the mononitroso-derivatives of resorcinol and orcinol appear to yield these colouring matters, the dinitroso-derivatives showing no such reaction.

When paramidophenolsulphonic acid is subjected to dry distillation, it yields a dark violet-coloured sublimate, which appears to be identical with Liebermann's phenol colouring matter,  $\text{C}_{18}\text{H}_{15}\text{HO}_3$ . Neither the ortho- nor the meta-compound give any such sublimate.

$\alpha$ -Amidoresorcinolsulphonic acid, obtained by the reduction and

subsequent sulphonation of Weselsky and Benedict's nitroresorcinol,  $[\text{OH} : \text{OH} : \text{NO}_2 = 1 : 3 : 4]$ , appears to be identical with the acid described by Hazura (Abstr., 1883, 1114), but the author's specimen crystallised in green lustrous scales, whilst Hazura's yielded reddish prisms. This acid when dry-distilled yields azoresorcinol or azoresorufin, according to the temperature employed.

*v*-Amidoresorcinolsulphonic acid, prepared from Weselsky and Benedict's nitroresorcinol,  $[\text{OH} : \text{OH} : \text{NO}_2 = 1 : 3 : 2]$ , and which therefore has not a hydroxyl-group in the para-position to the nitro-group, yields no colouring matter when heated. The acid crystallises in small colourless needles or prisms soluble in boiling water. Its solution reduces an ammoniacal silver solution in the cold.

From the results of their own and other investigators' work, the authors conclude that the nitrogen-atom in Liebermann's colouring matter is in the para-position to one of the hydroxyls, and that in polyhydric phenols only those can form these compounds in which two hydroxyl-groups are in the meta-position relatively to one another.

L. T. T.

**$\beta$ -Metaisocymenesulphonic Acid.** By W. KELBE and N. v. CZARNOMSKI (*Ber.*, 17, 1746—1748).—The author, some time ago, (Abstr., 1882, 619) described a bromisocymenesulphonic acid obtained by dissolving  $\beta$ -bromisocymene in fuming sulphuric acid. The author now finds that this acid yields  $\beta$ -metaisocymenesulphonic acid on reduction. He has proved the identity of this last-named acid with that obtained by direct sulphonation of isocymene by a comparison of their salts. The salts and derivatives prepared were:— $(\text{C}_{10}\text{H}_{13}\text{SO}_3)_2\text{Ba} + 8\text{H}_2\text{O}$ ;  $(\text{C}_{10}\text{H}_{13}\text{SO}_3)_2\text{Cu} + 3\frac{1}{2}\text{H}_2\text{O}$ ;  $\text{C}_{10}\text{H}_{13}\text{SO}_3\text{Na} + 3\text{H}_2\text{O}$ ;  $\text{C}_{10}\text{H}_{13}\text{SO}_3\text{NH}_4$  melting at  $162^\circ$ ;  $(\text{C}_{10}\text{H}_{13}\text{SO}_3)_2\text{Pb} + 8\text{H}_2\text{O}$ ;  $(\text{C}_{10}\text{H}_{13}\text{SO}_3)_2\text{Ca} + 5\frac{1}{2}\text{H}_2\text{O}$ .

When treated at  $40^\circ$  with bromine dissolved in hydrobromic acid, this acid yields principally a bromisocymenesulphonic acid crystallising with 3 mols.  $\text{H}_2\text{O}$ , together with small quantities of bromisocymene.

L. T. T.

**Behaviour of Tannin and Oak-bark Tannin towards Various Reagents.** By C. ETTL (*Ber.*, 17, 1820—1823).—When boiled with dilute sulphuric acid under ordinary pressure, tannin takes up water and forms gallic acid, whilst "oak-bark tannin" gives up water and forms an anhydride. The same effects are produced by solutions of the caustic alkalis, except that the anhydride produced is of a different nature. Heated with dilute sulphuric acid at  $130$ — $140^\circ$  under pressure, oak-bark tannin only gives traces of gallic acid. Tannin remains unchanged at  $200^\circ$ , oak-bark tannin loses a constant weight of water at  $130$ — $140^\circ$ , and is converted into an anhydride. With acetic anhydride, tannin forms acetotannins, whilst oak tannin gives anhydrides and acetylated anhydrides. When boiled with aqueous ammonia in an atmosphere of hydrogen, tannin yields gallamide and an acid ammonium gallate in almost theoretical quantity; oak tannin yields nothing but indefinite resinous compounds.

It is thus clear that these two compounds are not identical, and that oak bark does not contain ordinary tannin.

From the analogy of the formation of gallamide and ammonium gallate by the action of ammonia on tannin, to that of lactamide and ammonium lactate from the action of ammonia on lactic anhydride,  $\text{CHMe}(\text{OH})\cdot\text{COO}\cdot\text{CHMe}\cdot\text{COOH}$ , the author is inclined to look upon tannin as  $\text{C}_6\text{H}_2(\text{OH})_3\cdot\text{COO}\cdot\text{C}_6\text{H}_2(\text{OH})_2\cdot\text{COOH}$ . L. T. T.

### Synthesis of Diphenylethane from Ethylidene Chloride.

By R. D. SILVA (*Bull. Soc. Chim.*, **41**, 448—449).—Priority is claimed for the synthesis of diphenylethane from ethylidene chloride and benzene in presence of aluminium chloride, which has recently been announced by Angeblis and Anschütz (*Abstr.*, 1884, 753), the author's results having been published in 1881 (*Bull. Soc. Chim.*, **36**, 66). By passing the vapour of ethylidene chloride into a mixture of benzene and aluminium chloride heated at  $70^\circ$ , ethylbenzene is obtained as well as unsymmetrical diphenylethane, from which it differs by containing one  $\text{C}_6\text{H}_4$  residue less. This body is not formed in the preparation of symmetrical diphenylethane, but in the preparation of unsymmetrical diphenylpropane a notable quantity of cumene is obtained; this hydrocarbon stands in the same relation to diphenylpropane that ethylbenzene does to diphenylethane. W. R. D.

**Acridines.** By A. BERNTHSEN (*Annalen*, **224**, 1—56).—Most of the acridine and phenylacridine-derivatives have been previously described by the author (*Annalen*, **192**, 1; *Abstr.*, 1883, 580, 1099, 1133, 1134, 1183). The best yield of acridine is obtained by the action of zinc or aluminium chloride on a mixture of chloroform and diphenylamine.

In addition to the methods which have been previously given (*loc. cit.*), phenylacridine can also be prepared by acting on a mixture of diphenylamine and benzotrichloride with zinc chloride. Phenylacridine boils above  $400^\circ$ . Hydrophenylacridine easily loses 2 atoms of hydrogen. Phenylacridine yields *di*- and *tri*-nitro-derivatives, which are converted into the corresponding amido-compounds by reduction with tin and hydrochloric acid. The salts of these bases dye silk and wool. Phenylacridinedisulphonic acid, which has not yet been obtained in the pure state, dissolves in water, forming a brownish-yellow solution, which exhibits an intense green fluorescence. The sodium salt crystallises in colourless needles. It is decomposed by fusion with potash, yielding, amongst other products, a yellow colouring matter.

*Methylacridine*,  $\text{C}_{13}\text{H}_8\text{NMe}$ , melting at  $114^\circ$ , unites with methyl iodide, forming a crystalline compound which is deposited from aqueous or alcoholic solutions in red needles. The crystals melt at  $185^\circ$  with decomposition. *Dimethylacridinium hydroxide*,



forms a grey powder, which is decomposed by exposure to the air. The hydrochloride crystallises in prisms which are freely soluble in water. It melts with decomposition between  $130^\circ$  and  $135^\circ$ . Cautious



oxidation with potassium permanganate appears to convert methylacridine into quinolinetricarboxylic acid. Strong nitric acid transforms it into trinitroacridinecarboxylic acid,  $C_{13}H_5(NO_2)_3N.COOH$ . Butylacridine and acridylbenzoic acid have been already described (this vol., p. 1183).  
W. C. W.

**Phenyl- $\beta$ -naphthacridine.** By C. RUS (*Ber.*, **17**, 2029—2032).—

*Phenyl- $\beta$ -naphthacridine*,  $C_{27}H_{17}N = C_{10}H_6 \begin{array}{c} \diagup CPh \\ | \\ N- \end{array} \diagdown C_{10}H_6$ , is obtained

by heating a mixture of  $\beta$ -dinaphthylamine with three times its weight of benzoic chloride for eight hours at the boiling point of the mixture. It is also formed by the action of zinc chloride on benzoyldi- $\beta$ -naphthylamine at  $240^\circ$ , and on a mixture of  $\beta$ -dinaphthylamine and benzoic acid at  $280^\circ$ . It crystallises in nearly colourless needles, melts at  $297^\circ$ , and sublimes in needles. It is readily soluble in hot benzene and glacial acetic acid, sparingly soluble in ether and alcohol. 100 parts of alcohol at  $18^\circ$  dissolve 0.04 part, and 100 parts of benzene 0.29 of phenyl- $\beta$ -naphthacridine. The substance has been previously obtained by Claus and Richter (this vol., p. 1358). The *hydrochloride*,  $C_{27}H_{17}N.HCl$ , forms a yellow crystalline powder. The *platinochloride*,  $(C_{27}H_{17}N)_2.H_2PtCl_6$ , crystallises in brilliant yellow plates. The sulphate forms tufts of yellow crystals.  
A. J. G.

**The Question of the Ammonium Bases derived from Acridine and Quinoline.** By A. BERNTHSEN (*Ber.*, **17**, 1947—1957).—A reply to Claus (this vol., p. 1359), in which the author reaffirms the accuracy of the constitution assigned by him to methylphenylacridine-ammonium hydroxide (*Abstr.*, 1883, 1133), and criticises the views of Claus as to the nature of the bases obtained by the action of silver oxide on the alkyl haloid addition-products of quinoline.


A. J. G.

**Preparation of Propyl and Amyl-naphthalene.** By L. ROUX (*Bull. Soc. Chim.*, **41**, 379—382).—These compounds can be prepared by Friedel and Crafts' aluminium chloride reaction. 200 grams of naphthalene and 120 grams of  $\alpha$ -propyl bromide are heated in an apparatus with reflux condenser, and as soon as the mixture commences to distil 10 grams of aluminium chloride are added in very small quantities at a time. When the theoretical quantity of hydrobromic acid has been evolved, the mixture is cooled, and from 300—400 grams of carbon bisulphide added. The liquid is then treated with water, the carbon bisulphide decanted and distilled to dryness from a water-bath. The residue is fractionally distilled in a vacuum. In this way a highly refractive, aromatic liquid is obtained which boils at  $262$ — $267^\circ$ . It is insoluble in water, but soluble in benzene and alcohol. The purified compound crystallises from benzene or alcohol in slender yellow needles melting at  $89$ — $90^\circ$ . This hydrocarbon is probably isopropyl-naphthalene, for it has been shown that under the influence of aluminium chloride the propyl-group becomes an isopropyl-group. By a similar method, amyl-naphthalene is obtained from amyl chloride boiling at  $100$ — $102^\circ$ , and naphthalene. It is a colour-

less liquid boiling at 288—292°; the picric acid compound melts at 105—110°. This hydrocarbon appears to be isomeric with the two amyl-naphthalenes already obtained; the one by the action of hydriodic acid and phosphorus on lapachic acid, the picric acid compound of which melts at 140—141°; the other by Fittig's method, the picric acid compound of which melts at 85—90°. In the preparation of both propyl- and amyl-naphthalene, isodinaphthyl is formed by the reducing action of aluminium chloride. This secondary reaction occurs exclusively when amyl chloride is allowed to fall drop by drop into a mixture of 100 grams of naphthalene and 25 grams of aluminium chloride heated at 120°. Under these conditions pentane, boiling at 29—34°, and isodinaphthyl are formed according to the equation,  $2C_{10}H_8 + C_5H_{11}Cl = HCl + C_5H_{12} + (C_{10}H_7)_2$ , but no amyl-naphthalene.

W. R. D.

**Action of Phosphorus Pentachloride and Pentoxide on Benzoyl- $\beta$ -Naphthylphenylamine and on Benzoyldi- $\beta$ -naphthylamine.** By A. CLAUS and C. RICHTER (*Ber.*, 17, 1590—1597).—*Benzoyl- $\beta$ -naphthylphenylamine*,  $\beta$ - $C_{10}H_7$ .NPhBz, is readily obtained by heating a mixture of benzoic chloride and  $\beta$ -naphthylphenylamine at 50—60°; it crystallises from alcohol in colourless lustrous needles melting at 147—148°. It is insoluble in water, sparingly soluble in cold alcohol, readily in benzene and acetic acid. It is decomposed by boiling alcoholic potash, yielding benzoic acid in theoretical quantity, whilst the naphthylaniline is converted into a brown resinous mass. The action of phosphorus pentachloride on benzoyl- $\beta$ -naphthylphenylamine takes place much more readily than with the corresponding diphenyl-derivative (Abstr., 1882, 1060), and is best effected in chloroform solution; hydrochloric acid is evolved with formation of phosphorus trichloride, and the compound  $\beta$ - $C_{10}H_6$ Cl.NPhBz is produced. This is insoluble in water, soluble in alcohol, ether, chloroform, benzene, and glacial acetic acid; it crystallises in colourless needles melting at 152°. That the substitution takes place in the naphthyl-group is proved by the following facts:—On again treating the substance with the pentachloride, a higher chlorinated derivative is not formed; benzoyldi- $\beta$ -naphthylamine when treated as above is readily converted into a dichlorinated derivative, whilst benzoyldiphenylamine yields no substitution-derivative with phosphorus pentachloride unless the mixture is heated above 150° (*Ber.*, 15, 1285). *Benzoyldi- $\beta$ -naphthylamine*, ( $\beta$ - $C_{10}H_7$ )<sub>2</sub>NBz, obtained by heating  $\beta$ -dinaphthylamine with benzoic chloride at 120°, crystallises in white needles and melts at 173°. It yields benzoic acid and a resinous mass on saponification. The dichlorinated derivative, ( $\beta$ - $C_{10}H_6$ Cl)<sub>2</sub>NBz, crystallises from alcohol, benzene, and chloroform in small white needles melting at 203°; it also yields benzoic acid on treatment with alkalis.

By the action of phosphorus pentoxide on the  $\beta$ -naphthyl-derivative, water is abstracted and bases produced which belong to the acridine series. *Phenyl- $\beta$ -naphthacridine*,  $C_{10}H_6$    $C_{10}H_6$ , is obtained by extracting with potash solution the melt from dinaphthyl-

amine (1 part), benzoic acid (1 part), and phosphoric anhydride ( $1\frac{1}{2}$ —2 parts), the residue being then washed, dried, and sublimed. It forms bright yellow needles melting at  $294^{\circ}$ ; its basic properties are very feeble. The *hydrochloride* crystallises in long golden-red lustrous needles which are decomposed by water or alcohol; the *platinochloride*,  $(C_{27}H_{17}N)_2, H_2PtCl_6$ , forms yellow needles, and the *chromate* reddish-

brown needles. *Phenylbenzo- $\beta$ -naphthacridine*,  $C_6H_5 \begin{array}{c} \diagup N \diagdown \\ | \\ CPh \end{array} C_{10}H_6$ , ob-

tained from  $\beta$ -naphthylphenylamine and benzoic acid, sublimes in almost colourless needles melting at  $198^{\circ}$ . The *hydrochloride* melts at  $235^{\circ}$ , and can be crystallised from water or alcohol containing a little free acid; the *platinochloride*,  $(C_{23}H_{15}N)_2, H_2PtCl_6$ , forms lustrous yellow needles. When the above bases are heated in sealed tubes with methyl iodide, both yield compounds crystallising in red needles. No additive product, however, could be obtained from phenylacridine and benzyl chloride even at  $200^{\circ}$ , whilst at  $210$ — $220^{\circ}$  phenylacridine hydrochloride is produced. In conclusion, the authors object to the view held by Bernthsen (*Annalen*, **124**, 1), that the alkyl-derivatives of phenylacridine are quaternary ammonium bases. A. K. M.

**Orthonitrosonaphthols.** By H. GOLDSCHMIDT and H. SCHMID (*Ber.*, **17**, 2066—2069).—Goldschmidt has shown (this vol., 735 and 1137) that both  $\beta$ -nitroso- $\alpha$ -naphthol and  $\alpha$ -nitroso- $\beta$ -naphthol are converted by the action of hydroxylamine hydrochloride at  $150^{\circ}$  into

a substance of the formula  $C_{10}H_6 \begin{array}{c} N \\ \diagdown \quad \diagup \\ O \end{array}$  [1 : 2], that must be re-

garded as the anhydride of a body derived from naphthalene dihydride by replacement of 4 hydrogen-atoms by 2 isonitroso-groups. The authors have succeeded in isolating this isonitroso-compound by the action of hydroxylamine hydrochloride on both the orthonitrosonaphthols at the temperature of  $100^{\circ}$ . *Diisonitrosonaphthalene dihydride*,  $C_{10}H_8N_2O_2 = C_{10}H_6(NO)_2$ , [1 : 2] crystallises in yellow needles, melts at  $149^{\circ}$ , but shows signs of decomposition at  $140^{\circ}$ ; is soluble in hot water and benzene. It dissolves in alkalis with reddish-yellow colour, yields a red sodium salt, and an orange-red silver salt. It dissolves in concentrated sulphuric acid with a dark-brown coloration; the compound is reprecipitated on adding water. It is readily converted into the anhydride,  $C_{10}H_6N_2O$ , by the action of acetic chloride by heating the solution in sulphuric acid, or still more readily by heating the solution in alkalis.

The two orthonitrosonaphthols do not behave alike towards alkaline solutions of hydroxylamine,  $\alpha$ -nitroso- $\beta$ -naphthol giving mainly the anhydride  $C_{10}H_6N_2O$ , whilst with  $\beta$ -nitroso- $\alpha$ -naphthol little more than a trace of this compound is obtained. A. J. G.

**Phenylhydrazine-derivatives of Hydroxynaphthaquinone.** By T. ZINCKE and H. THELEN (*Ber.*, **17**, 1809—1813).—When a cold alcoholic solution of hydroxynaphthaquinone is mixed with a cold,

aqueous, alcoholic, or acetic solution of phenylhydrazine, *hydroxynaphthaquinonehydrazine*,  $C_{10}H_5(OH)O:N_2HPh$ , is formed. It crystallises in glistening orange crystals which are easily soluble in ether, boiling alcohol, or acetic acid, and melts with decomposition at  $230^\circ$ . It forms well characterised compounds with metals, alcohol radicles, and acetyl. The *barium* derivative, prepared by precipitating the ammoniacal solution of the hydrazide with barium chloride, crystallises in brownish-gold scales or long red needles soluble in alcohol: the first-named form is the less stable and usually passes gradually into the needles. Their formula is  $(C_{16}H_{11}N_2O_2)_2Ba + 10H_2O$ . When dehydrated by heating, it is insoluble in alcohol, but is rendered soluble again by moistening. The *sodium* salt crystallises in small orange needles soluble in alcohol; the *calcium* salt forms orange needles; the *silver* salt a reddish-brown amorphous precipitate which immediately blackens on heating. The other metallic salts are orange or red precipitates, the *lead* and *mercury* salts being insoluble in alcohol. The *acetate*,  $C_{10}H_5(OAc)O:N_2HPh$ , formed by boiling the hydrazide with acetic anhydride, forms long red needles melting at  $178-179^\circ$ , and soluble in alcohol and boiling acetic acid. The *ethyl-derivative*,  $C_{10}H_5(OEt)O:N_2HPh$ , is formed by treatment of an alcoholic solution of the potassium salt with ethyl bromide, by boiling the free hydrazide with alcohol and sulphuric acid, or by heating it with alcohol and ethyl iodide. It forms orange needles which are easily soluble in boiling alcohol and acetic acid, and melt at  $172-173^\circ$ . The *methyl-derivative* forms small red needles melting at  $174-175^\circ$ . When an alcoholic solution of the hydrazide is boiled with benzaldehyde, a deep-red crystalline compound of the formula



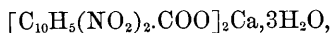
is formed. It is sparingly soluble in the usual solvents, and forms well characterised metallic derivatives, the *potassium* and *sodium* derivatives crystallising in small orange needles soluble in alcohol. When suspended in carbon bisulphide, the hydrazide may be easily brominated, and if equal molecular weights of bromine and the base are used, *monobromohydroxynaphthaquinonehydrazine* is formed: this crystallises in dark-red needles which melt with decomposition at  $196-198^\circ$ , and are easily soluble in boiling acetic acid, sparingly so in alcohol. It forms metallic derivatives, and as it is not decomposed by dilute acids or alkalis the position of the bromine could not be determined. Strong hydrochloric acid decomposes it, but the reaction is of a complex character, dark coloured, amorphous, and uncrystallisable compounds being formed.

As the hydrazide is so easily converted into the ether by boiling with alcohol and sulphuric acid, the same reaction was tried with hydroxynaphthaquinone, when the authors found that here also the formation of the ether took place readily.

L. T. T.

**Derivatives of Naphthoic Acid.** By A. G. EKSTRAND (*Ber.*, **17**, 1600—1605).—By the action of fuming nitric acid on  $\alpha$ -naphthoic acid, a mixture is obtained from which the author has succeeded in isolating a *dinitro- $\alpha$ -naphthoic acid*,  $C_{10}H_5(NO_2)_2.COOH$ ; this melts at

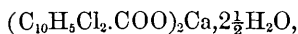
263—265°, crystallises from alcohol in small prisms or needles, dissolves readily in warm alcohol and glacial acetic acid, sparingly in ether and benzene, slightly also in hot water. On sublimation, it is obtained in yellowish-white needles. The *calcium salt*,



crystallises in needles moderately soluble in warm, sparingly in cold water (1 in 138). The *ethyl-derivative*,  $\text{C}_{10}\text{H}_5(\text{NO}_2)_2.\text{COOEt}$ , crystallises from alcohol in slender needles melting at 143°. The dinitronaphthoic acid (or acids) is accompanied by an indifferent substance, which appears to be dinitronaphthalene. It is separable by alcohol into two portions, the more soluble of which melts at 155—160°, and the less soluble at 170°. When  $\beta$ -naphthoic acid is treated in the same way as the  $\alpha$ -acid, it yields a mixture of *dinitro- $\beta$ -naphthoic acids*, but no dinitronaphthalene. By crystallisation from alcohol and mechanical separation of the different forms of crystals, two dinitro- $\beta$ -naphthoic acids have been isolated. One of these melts at 226°, crystallises in long slender silky needles, and dissolves readily in alcohol, ether, and glacial acetic acid, sparingly in benzene; its *ethyl salt*,  $\text{C}_{10}\text{H}_5(\text{NO}_2)_2.\text{COOEt}$ , melts at 141°, forms long silky needles readily soluble in warm alcohol. The second *dinitro- $\beta$ -naphthoic acid* melts at 248°, and crystallises in small hard rectangular prisms; it is readily soluble in warm alcohol, glacial acetic acid, and ether, sparingly in benzene; the *calcium salt* forms prismatic needles, moderately soluble in hot water; the *ethyl salt*,  $\text{C}_{10}\text{H}_5(\text{NO}_2)_2.\text{COOEt}$ , forms small hard wedge-shaped crystals melting at 165°, and sparingly soluble in alcohol. *Monochloro- $\alpha$ -naphthonitrile*,  $\text{C}_{10}\text{H}_6\text{Cl.CN}$ , is obtained by passing chlorine into a solution of  $\alpha$ -naphthonitrile in carbon bisulphide to which some iodine has been added. It crystallises from alcohol in needles melting at 145°. On heating it with concentrated hydrochloric acid in a sealed tube, *chloro- $\alpha$ -naphthoic acid*,



is obtained, and crystallises in colourless lustrous needles, readily soluble in alcohol, sparingly in glacial acetic acid and in benzene; this acid is also formed by the action of chlorine, in the presence of iodine, on a solution of  $\alpha$ -naphthoic acid in glacial acetic acid. The *calcium salt*,  $(\text{C}_{10}\text{H}_6\text{Cl.COO})_2\text{Ca}, 2\text{H}_2\text{O}$ , forms colourless needles, soluble in 116 parts water at the ordinary temperature; the *ethyl-derivative*,  $\text{C}_{10}\text{H}_6\text{Cl.COOEt}$ , crystallises in quadrangular plates melting at 42°. *Dichloro- $\beta$ -naphthoic acid*,  $\text{C}_{10}\text{H}_5\text{Cl}_2.\text{COOH}$ , is prepared by passing chlorine in excess into a solution of  $\beta$ -naphthoic acid in glacial acetic acid containing also iodine; the crystals are separated from the mother-liquor and boiled with alcohol; the residue consisting of dichloronaphthoic acid melts at 291°, is very sparingly soluble in alcohol, and still less soluble in glacial acetic acid; it crystallises in colourless needles. One or more other and more readily soluble chlorine-derivatives are also produced. The *calcium salt*,



of the above acid forms small prisms, soluble in 3018 parts of water

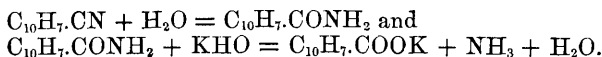
at the ordinary temperature; the *ethyl salt*,  $C_{10}H_5Cl_2.COOEt$ , crystallises in long needles melting at  $66^\circ$ .

A. K. M.

**Amides of  $\alpha$ - and  $\beta$ -Naphthoic Acids.** By T. LEONE (*Gazzetta*, **14**, 120—124).—Rakowski (*Ber.*, **5**, 318) found that the product insoluble in water, obtained in the saponification of  $\alpha$ -cyanonaphthalene with alcoholic potash, is not naphthalene, as Merz and Mulhäuser supposed (*ibid.*, **3**, 709), but the amide of  $\alpha$ -naphthoic acid, and he gives the melting point as  $128^\circ$ , whilst Hofmann (*Compt. rend.*, **66**, 476) gives the melting point of the amide as  $207^\circ$ .\* The author having occasion to prepare a large quantity of naphthoic acids determined to clear up the discrepancy.

The  $\alpha$ -cyanonaphthalene employed was prepared by distilling an intimate mixture of potassium ferrocyanide and  $\alpha$ -naphthalenesulphonate in equal parts; the crude distillate was boiled with alcoholic potash until ammonia ceased to be given off, the alcohol evaporated, and the residue taken up with water. Only a very small portion remained undissolved, and this, when distilled with water, yielded naphthalene, which passed over with the steam, and a residue containing sulphur, but no nitrogen; this substance was proved to be originally present in the crude cyanonaphthalene. If pure  $\alpha$ -cyanonaphthalene be used there is no residue if the digestion with alcoholic potash be continued until ammonia is no longer given off; this requires some days. If, however, the action is not continued so far, there is a product formed, insoluble in water, and which, on examination, was found to be the amide of  $\alpha$ -naphthoic acid,  $C_{10}H_7.CONH_2$ . It forms colourless needles which, after being carefully purified, melt at  $202^\circ$ . The author finds that the saponification of the nitrile takes place in two stages; it is first converted into the amide, and this is subsequently decomposed, yielding  $\alpha$ -naphthoic acid and ammonia; by stopping the action at the proper time the whole of the nitrile will be found to be transformed into the amide.

This is represented in the equations:—



The  $\beta$ -cyanonaphthalene was prepared in like manner to the  $\alpha$ -derivative, and the action of alcoholic potash on it is perfectly similar but more rapid. The amide of  $\beta$ -naphthoic acid obtained by stopping the action before saponification is complete, crystallises in plates which melt at  $192^\circ$ , and are soluble in alcohol, ether, benzene, &c. It is in every respect identical with the compound described by Vieth (*Annalen*, **180**, 320).

C. E. G.

**Dinaphthylsulphone.** By A. W. HOFMANN (*Ber.*, **17**, 1921—1922).—The author has succeeded in isolating the  $\beta$ -dinaphthylsulphone of Stenhouse and Groves from the bye-products obtained in

\* In *Ber.*, **1**, 38, Hofmann gives the melting point as  $244^\circ$ . This appears to be a typographical error, but unfortunately it has been reproduced in most of the text-books.—C. E. G.

the preparation of naphthalenesulphonic acid; their  $\alpha$ -dinaphthylsulphone was also obtained, but only in small quantity. L. T. T.

**Wormseed Oil.** By C. HELL and H. STÜRCKE (*Ber.*, **17**, 1970—1975).—The ethereal oil of wormseed, the flower buds of *Artemisia Vahlana*, has been submitted to numerous investigations with varying results; in particular, Kraut and Wahlfors (*Annalen*, **128**, 293) found the chief constituent to be an oil,  $C_{10}H_{18}O$ , converted by phosphoric anhydride into cynene,  $C_{10}H_{16}$ , whilst Faust and Homeyer (this Journal, 1875, 371) found the product of the action of phosphoric anhydride to be identical with cymene, thus giving the parent compound the formula  $C_{10}H_{16}O$ .

The fraction of wormseed oil distilling between  $172^{\circ}$ — $175^{\circ}$  was rectified over soda; it then boiled constantly at  $172.5^{\circ}$ — $173^{\circ}$ , and had a very faint yellow colour. By renewed distillation over sodium, it was obtained absolutely colourless, and then boiled at  $172.6^{\circ}$  (uncorr.), and had a sp. gr. of 0.9255 at  $16^{\circ}$ . A part of the oil was still further purified by treatment with potassium permanganate, distillation with steam, and rectification over sodium; it boiled at  $172.5^{\circ}$  (uncorr.), had the sp. gr. 0.9275 at  $16^{\circ}$ , 0.8981 at  $50^{\circ}$ , and 0.8553 at  $100^{\circ}$ . On analysis it gave numbers agreeing with the formula  $C_{10}H_{18}O$ . Vapour-density determination gave 4.98 and 5.03, calc. for  $C_{10}H_{18}O = 5.33$ . When heated with phosphoric anhydride, it yielded a small quantity of hydrocarbons boiling between  $120^{\circ}$ — $166^{\circ}$ , apparently paraffins, cynene, and polymerised cynenes, mainly dicynene. *Cynene*,  $C_{10}H_{16}$ , is a mobile colourless liquid of aromatic odour, recalling that of oil of lemons; it boils at  $174.5^{\circ}$  under 731 mm. pressure (uncorr.), has sp. gr. 0.85 at  $15^{\circ}$ , 0.8238 at  $50^{\circ}$ , and 0.7851 at  $100^{\circ}$ . Vapour-density = 4.35, calc. = 4.7. On mixing cynene with concentrated sulphuric acid (slightly fuming) the liquid becomes dark brown, and, especially on heating, sulphurous anhydride is freely evolved; the sulphonic acid formed was found to be *cymenesulphonic acid*, thus explaining the results obtained by Faust and Homeyer.

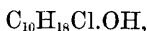
*Dicynene*,  $C_{20}H_{32}$ , is a yellowish oil of pale blue fluorescence. It distils between  $328^{\circ}$ — $333^{\circ}$ ; vapour-density = 9.1 and 9.2 calc. = 9.4.

A. J. G.

**Action of the Haloïd Acids on Wormseed Oil.** By C. HELL and A. RITTER (*Ber.*, **17**, 1975—1980).—By the action of hydrochloric acid gas at  $10^{\circ}$ — $12^{\circ}$  on the fraction of wormseed oil distilling between  $172^{\circ}$  and  $173^{\circ}$  (see preceding Abstract), a mass of prismatic or tabular crystals is obtained. Analysis confirms the formula,  $C_{10}H_{18}O.HCl$ , assigned to the compound by Volckel (*Annalen*, **87**, 315). It melts at  $30^{\circ}$ — $35^{\circ}$ ; loses hydrochloric acid on exposure to air, and is decomposed into its components by heating or by treatment with water. At high temperatures, the reaction takes a different course, cynene dihydrochloride being formed with separation of water; the best yield of the hydrochloride is obtained at  $40^{\circ}$ — $50^{\circ}$ .

*Cynene dihydrochloride*,  $C_{10}H_{16}Cl_2$ , crystallises in colourless silky lancet-shaped tables, melts at  $50^{\circ}$ — $51^{\circ}$ , is soluble in alcohol, ether, chloroform, benzene, light petroleum, and glacial acetic acid. It is stable in air, and is not decomposed by water. It has a camphor-like

odour, and volatilises completely at ordinary temperatures. On dry distillation it is decomposed into cynene and hydrochloric acid; it also yields cynene on long boiling with water or aqueous potash. The action of hydrochloric acid on wormseed oil is therefore represented by the equations:  $C_{10}H_{18}O + HCl = C_{10}H_{18}Cl.OH$  and  $C_{10}H_{18}Cl.OH + HCl = C_{10}H_{18}Cl_2 + H_2O$ . The formation of the compound,



seems to show the absence of a CO-group in wormseed oil, and this is further confirmed by the indifference of the oil towards hydroxylamine; it is very probable that the oxygen is in a state of union similar to that in which it occurs in ethylene oxide. A. J. G.

**Camphor.** By H. GOLDSCHMIDT and R. ZÜRRER (*Ber.*, **17**, 2069—2073).—Nägeli has shown (*Abstr.*, 1883, 728; this vol., 610 and 1190) that camphor is converted by hydroxylamine into camphoroxime,  $C_{10}H_{17}NO$ , this, by the action of acetic chloride into an anhydride,  $C_{10}H_{15}N$ , which, finally by heating with alcoholic potash, is converted into isocamphoroxime. The authors show that the last two compounds are respectively the nitrile and the amide of a new acid, campholenic acid. The anhydride (nitrile),  $C_{10}H_{15}N$ , like other nitriles, unites with hydroxylamine to form a compound,  $C_{10}H_{18}N_2O$ , crystallising in white plates and melting at  $101^\circ$ . It is soluble both in acids and in alkalis.

*Campholenic acid*,  $C_9H_{15}.COOH$ , is prepared from the nitrile,  $C_{10}H_{15}N$ , by long boiling with alcoholic potash, &c. It is a colourless oil of a peculiar odour, boils at  $254$ — $255^\circ$ , is insoluble in water, and has marked acid properties. It is isomeric with Montgolfier's camphic acid (*Abstr.*, 1878, 891). The ammonium salt is converted into isocamphoroxime by heating it for some hours at  $150^\circ$ . Isocamphoroxime is converted into the nitrile,  $C_{10}H_{15}N$ , by distillation with phosphoric sulphide.

In the expectation that carboxime would behave like camphoroxime, it was treated with acetic chloride, but was found to yield not an anhydride but an acetyl-derivative,  $C_{10}H_{14}NOAc$ , a yellow oil decomposing on heating. A. J. G.

**Sylvic and Pimaric Acids.** By C. LIEBERMANN (*Ber.*, **17**, 1884—1887).—Sylvic and pimaric acids, when dissolved in acetic anhydride and treated with sulphuric acid, give a very similar colour reaction to quinovic acid, except that the shade is bluer and rather more evanescent.

When treated with hydriodic acid and amorphous phosphorus, these bodies behave in a manner similar to pyroquinovic acid. The hydrocarbon produced is a colourless thick liquid, boiling between  $320^\circ$  and  $330^\circ$ , but always with slight decomposition. In properties, it resembles Deville's colophene (*Annalen*, **37**, 162), produced by the dry distillation of colophonium. The analytical results are very close to those required for colophene, but agree better for the formula  $C_{20}H_{34}$ . The hydrocarbons obtained from pimaric and sylvic acids are identi-

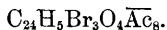


cal in all their properties except their rotatory power. These acids may, therefore, be considered to be derivatives of a terpene.

Kraut has lately obtained a new acid from a Siamese gum-benzoin, which resembles sylvic and pimaric acids in some respects, but differs from them in composition and melting point, which lies above  $100^{\circ}$ . With hydriodic acid, it gives a terpene ( $C_{10}H_{16}$ ) which is solid in the cold, and boils above  $360^{\circ}$ .  
L. T. T.

**Juglone.** By A. BERNTHSEN (*Ber.*, 17, 1945—1947).—*Juglone* or *Nucin* has been studied by Reischauer and Vogel (*Abstr.*, 1878, 233), who assign to it the formula  $C_{18}H_{12}O_6$ . Their analytical results, and also the author's, agree much better with either  $C_{14}H_8O_4$  or  $C_{10}H_6O_3$ , and the latter would appear to be correct, as juglone is apparently a hydroxynaphthaquinone. It crystallises in long brilliant clear red needles, and melts at  $145$ — $147^{\circ}$ . On distilling juglone with zinc-dust, it yields naphthalene (?) It resembles the quinones in its behaviour, being converted into a substance of phenol-like nature on reduction with zinc and hydrochloric acid, stannous chloride, or sulphurous acid. This substance is soluble in alkalis, and is then readily reoxidised. Aniline reacts with juglone in a manner similar to its behaviour with ordinary hydroxynaphthaquinone, forming a red substance soluble in alcohol. Juglone crystallises unaltered from dilute nitric acid; acid of sp. gr. 1.15 converts it into a readily soluble acid. Reischauer's analysis of the copper-compound of juglone agrees better with the formula  $(C_{10}H_6O_3)_2Cu$  than with  $C_{18}H_{10}O_6Cu$ , the formula he assigned to it.  
A. J. G.

**Derivatives of Quercetin.** By C. LIEBERMANN (*Ber.*, 17, 1680—1684).—It has been shown by Herzig (this vol., p. 846) that quercetin can be converted into a hexamethyl- and hexethyl-quercetin, and these further into diacetyl-derivatives; he concluded, therefore, that quercetin contains eight hydroxyl-groups, and assumed that the acetyl-derivative described by Liebermann and Hamburger (*Ber.*, 12, 1178) is an octacetyl-quercetin, and not a diacetyl-compound as stated by them. The author has repeated his previous experiments, and by decomposing the acetyl-derivative by means of dilute sulphuric acid, and then weighing the recovered quercetin, he obtains results agreeing with the octacetyl-compound, thus confirming Herzig's experiments. The percentage of carbon and hydrogen also agrees better with octacetyl- than with diacetyl-quercetin. The author has also re-examined the compounds previously described as dibromo-quercetin and dibromodiacetyl-quercetin, and finds them to be respectively *tribromo-quercetin*,  $C_{24}H_{13}Br_3O_{11}$ , and *tribromooctacetyl-quercetin*,



A. K. M.

**An Alcohol from Birdlime.** By J. PERSONNE (*Compt. rend.*, 98, 1585—1587).—Birdlime is obtained by the fermentation, under special conditions, of the inner bark of the holly, and is a greenish, viscous, tenacious substance. When dried at  $100^{\circ}$ , it loses 26—27 per cent. of water, and if the residue is treated with chloroform or light petroleum, about 23 per cent. of vegetable and inorganic matter, consisting mainly

of calcium phosphate, remains undissolved. The solution is evaporated to dryness, and the residue heated at  $120^{\circ}$  for some time to expel the last traces of the solvent.

The purified birdlime thus obtained is an ethereal salt or a mixture of ethereal salts of an alcohol which seems to be homologous with benzylic alcohol. In order to isolate this alcohol, the birdlime is subjected to prolonged treatment with alcoholic potash. An elastic substance resembling caoutchouc, and soluble in chloroform, separates out, and the liquid portion is poured into a large quantity of water. The gelatinous matter which separates is washed with water, treated with acetic acid to remove traces of alkali, again washed with water, dissolved in boiling alcohol of  $90^{\circ}$ , and purified by filtration through animal charcoal and repeated crystallisation from boiling alcohol.

The alcohol thus obtained crystallises in slender silky needles, insoluble in cold water, but soluble in all proportions in boiling light petroleum, alcohol of  $90^{\circ}$ , chloroform, and ordinary ether. It is almost insoluble in alcohol of  $80^{\circ}$ , but its solubility increases with the concentration of the alcohol. It melts at  $175^{\circ}$ , sublimes at  $115^{\circ}$  under a pressure of 100 mm., and boils above  $350^{\circ}$ . Its vapours have no aromatic odour. The new alcohol, which the author calls *ilicic alcohol*, has the composition  $C_{25}H_{44}O$ . It yields an acetate melting at  $204-206^{\circ}$ , and exists in the birdlime in combination with one or several acids, which seem to belong to the fatty series. C. H. B.

**The Bitter Principle of Hops.** By H. BUNGENER (*Bied. Centr.*, 1884, 431).—The author has succeeded in isolating from the lupulin of hops, a crystalline body which is insoluble in water, and possesses all the properties of the acid obtained by Lemers. The lupulin is cleansed from coarser impurities by passing it through a sieve, then digested with light petroleum for 24 hours in a stoppered flask, the dark solution filtered off by the aid of suction, and distilled down until a dark brown liquid remains in the flask; on cooling, this solidifies to a crystalline cake, which after purification by several recrystallisations becomes an almost colourless mass. It melts at  $92-93^{\circ}$ . It is easily soluble in alcohol, ether, benzene, chloroform, carbon bisulphide, and glacial acetic acid, less so in cold petroleum, and not at all in water. Analysis agrees best with the formula  $C_{25}H_{35}O_4$ . J. F.

**Artificial Production of Diastase.** By C. SCHNEIDER (*Bied. Centr.*, 1884, 432).—The diastase formed during the changes which take place in albumin while the seed corn is germinating, has been assigned a formula by some experimentalists, the author thinks incorrectly. He doubts if the soluble ferments which we call diastase have a definite composition, and thinks our knowledge of the substance meagre, and its artificial production a remote possibility. J. F.

**Chlorophyll.** By A. MAYER (*Bied. Centr.*, 1884, 390—394).—The author names the true chlorophyll corpuscles trophoplasts, and the colourless trophoplasts he names anaplasts, which last compre-

hends the starch formers of Schimper, and in order to distinguish the morphological relation between the organs, the colouring corpuscles receive the name of chromoplasts, and the chlorophyll that of autoplasts. The anoplasts are found in those plant cells which are in darkness, or in relatively feeble light if the plant is under the influence of direct light; the presence of colourless trophoplasts in the epidermis cells of plants growing in full light leads to the belief that it is here the transformation of the chlorophyll corpuscle takes place, and that it is intimately connected with the amount of light present. There are, however, some unaccountable exceptions: the anoplasts are found abundantly in the cells of the unlighted portion of the plant, both in presence and absence of starch corpuscles. The coloured trophoplasts or chromoplasts exist abundantly in the flower leaves, adding to the attractions which lead to fertilisation by insects. In appearance they are generally round, but often spindle-shaped. There appear to be only two colours, yellow and orange, all the others being formed from them by action on the other constituents of the cell. The author declares the lipochlor of Pringsheim to be non-existent, and the hypochlorin of the same observer to be identical with chlorophan, but agrees with Pringsheim's view of the structure of the autoplasts. Crystalloid bodies of a long needle-like spindle form are often found in connection with the anoplasts. Schimper considers these bodies as the actual anoplasts, the author, as being a product of them and starch corpuscles.

The spindle-shaped substances which are found in the chloroplasts are stages in the transformation of the colour-substance (xanthophyll). The condition of those bodies is changeable, the autoplasts increasing by fissure. J. F.

**Chlorophyll.** By A. F. W. SCHIMPER (*Bied. Centr.*, 1884, 394—396).—The author differs from Mayer in some of his views respecting chlorophyll, particularly as regards the crystalloid bodies found both in the coloured and colourless corpuscles. According to Meyer they are a reserve of nitrogenous matter obtained from the plastide; Schimper declares them to be that substance itself. J. F.

**Action of Alkaline Hypochlorites and Hypobromites on Pyrroline.** By G. CIAMICIAN and P. SILBER (*Ber.*, 17, 1743—1745)—10 grams pyrroline were added slowly with constant agitation to 1 litre of a solution of sodium hypochlorite containing 50 grams of active chlorine. The solution was allowed to remain for some hours, and was then steam-distilled. A mixture of unchanged pyrroline and chlorinated pyrrolines passed over. The residual liquid was acidified with dilute sulphuric acid, and again steam-distilled, when tetrachloropyrroline passed over. The residue from this second distillation was filtered from separated carbon, and then extracted with ether. On evaporating the etheric solution, dichloromaleic acid is left; this yielded dichloromaleic anhydride on distillation.

When treated with potassium hypobromite, pyrroline yields brominated pyrrolines, together with dibromo-maleinimide. L. T. T.

**Synthesis of Pyrroline-derivatives. II.** By L. KNORR (*Ber.*, 17, 1635—1642).—The author previously described the formation of *phenyl-β-imidobutyric acid*,  $\text{NPh}:\text{CMe}.\text{CH}_2.\text{COOH}$ , by the condensation of aniline with ethyl acetoacetate (this vol., p. 1198), and this led him to assume the probability of Duisberg's ethyl paramidoacetoacetate (obtained from ammonia and ethyl acetoacetate), being *ethyl β-imidobutyrate*,  $\text{NH}:\text{CMe}.\text{CH}_2.\text{COOEt}$ . To test this he has examined the action of nitrous acid on the two compounds.

Phenyl-β-imidobutyric acid is converted by nitrous acid into *isonitrosoanilacetone*,  $\text{NPh}:\text{CMe}.\text{CH}:\text{NOH}$ . This crystallises in splendid white needles, melting at  $180^\circ$ ; it dissolves readily in ether and hot alcohol, sparingly in cold alcohol, and is insoluble in water, acids, and alkalis; it is not attacked by boiling hydrochloric acid, and is distinguished from isonitrosoacetone by its insolubility in alkalis. When heated above its melting point, it detonates. When ethyl β-imidobutyrate, prepared according to Duisberg's instructions, is submitted to the action of nitrous acid, ethyl isonitroso-β-imidobutyrate,  $\text{NH}:\text{CMe}.\text{C}(\text{NOH}).\text{COOEt}$ , is obtained, and on reducing this with zinc-dust and acetic acid *ethyl dimethylpyrrolinedicarboxylate*,  $\text{C}_{12}\text{H}_{17}\text{NO}_4$ , is formed; this melts at  $130^\circ$ , is insoluble in water, acids, and alkalis, moderately soluble in alcohol and ether. On saponification with alcoholic potash, potassium ethyl dimethylpyrrolinedicarboxylate is obtained as the chief product, together with a small quantity of potassium dimethylpyrrolinedicarboxylate. If the saponification be effected at  $150$ — $160^\circ$  in sealed tubes, dimethylpyrroline is obtained. The *monethylic dimethylpyrrolinedicarboxylate* crystallises in slender needles, melting above  $200^\circ$  with evolution of carbonic anhydride; it is insoluble in water, sparingly soluble in cold, moderately in hot alcohol and ether; the lead and silver salts form white amorphous precipitates. *Dimethylpyrrolinedicarboxylic acid* crystallises from water or ether in dense lustrous prisms; it is moderately soluble in water and alcohol, less so in ether; it melts at  $197^\circ$ , with violent evolution of carbonic anhydride; its lead and silver salts are crystalline. *Dimethylpyrroline*,  $\text{C}_6\text{H}_9\text{N}$ , after purification by distillation in steam, forms a nearly colourless oil, having an odour resembling that of chloroform, is almost insoluble in water, but readily soluble in alcohol and ether; it combines with mercuric chloride, and is converted by acids into a brownish-red resin. It is uncertain whether it is isomeric or identical with the dimethylpyrroline obtained by Weidel and Ciamician from animal tar.

The author finds that on reducing ethyl isonitrosoacetoacetate by means of zinc-dust and acetic acid, a compound is obtained melting at  $134^\circ$ , and strongly resembling ethyl dimethylpyrrolinedicarboxylate. Its composition agrees with the formula  $\text{C}_{12}\text{H}_{16}\text{O}_5$ , but further experiments are necessary to prove it to be a furfurane-derivative.

A. K. M.

**Pyridine-derivatives.** By W. KOENIGS and R. GEIGY (*Ber.*, 17, 1832—1838).—In a former communication (this vol., p. 1195), the authors described the formation of a mixture of di- and tri-chloropyridine by the action of phosphoric chloride at  $200^\circ$  on anhydrous barium pyridinedisulphonate. The dichloropyridine is found chiefly

in the aqueous part of the distillate, and is purified by help of its mercuriochloride. *Dichloropyridine*,  $C_5H_3NCl_2$ , crystallises in silky scales which melt at  $66-67^\circ$ . It is freely soluble in alcohol, moderately so in water. It has slightly basic properties, dissolves readily in hydrochloric acid, and with mercuric chloride forms a compound which crystallises in long needles. It is easily soluble in boiling alcohol, and melts at  $183^\circ$ . The *platinochloride*,



forms yellow needles. The crystalline portion of the distillate from the action of phosphoric chloride consists chiefly of *trichloropyridine*, which melts at  $49-50^\circ$ , and crystallises in long flat needles, easily soluble in boiling alcohol, almost insoluble in water. It has much feebler basic properties than dichloropyridine, and is almost insoluble in hydrochloric acid. It forms a compound with mercuric chloride which melts, with decomposition, at  $209^\circ$ , and is easily soluble in boiling alcohol, insoluble in water. When trichloropyridine is boiled with sodium ethylate, *dichlorethoxyppyridine*,  $C_5H_2NCl_2 \cdot OEt$ , is formed; this is volatile in steam, and the crystals melt at  $31^\circ$ . From analogy to the easy replacement of chlorine by ethoxyl in  $\alpha$ -chloroquinoline, the authors are inclined to consider that the third chlorine-atom in trichloropyridine occupies the  $\alpha$ -position. *Monhydroxydichloropyridine* is obtained by the saponification of the ethoxy-compound with hydrochloric acid at  $150^\circ$ . It forms long lanceolate crystals, melts at  $171^\circ$ , and is easily soluble in boiling water, in alkalis, alkaline carbonates, and acids. It gives no coloration with ferric chloride, but gives a precipitate with silver nitrate. *Dihydroxyppyridine*,  $C_5H_3N(OH)_2$ , is obtained by fusing potassium pyridinedisulphonate with potash. It crystallises from water in long yellow needles, with  $\frac{1}{2}H_2O$ . The anhydrous compound melts at  $255^\circ$ , and is sparingly soluble in alcohol and the other usual solvents, but dissolves readily in acids and alkalis. An aqueous solution gives an intense brownish-red coloration with ferric chloride, whilst with phosphotungstic acid it yields a yellow precipitate soluble in boiling water. With mercuric and cadmium chlorides, lead acetate, and silver nitrate, it forms white, sparingly soluble compounds. The *hydrochloride*,  $C_5H_3NO_2 \cdot HCl$ , crystallises in yellow needles, easily soluble in alcohol and water. Blackening and decomposition begin at  $140^\circ$ , but the mass only completely melts at  $207^\circ$ . The *neutral sulphate* forms deliquescent plates. Platinic and auric chlorides yield no precipitates. The *sodium salt* produces sparingly soluble precipitates with lead, calcium, barium, and silver salts; the silver salt blackens very quickly. When dihydroxyppyridine is heated with zinc-dust, a strong odour of pyridine is produced, but it is scarcely acted on by sodium-amalgam, or by tin and hydrochloric acid.

The mother-liquors from the preparation of barium pyridinedisulphonate were converted into the potassium salt, and this salt, when fused with potash, yielded  $\beta$ -hydroxyppyridine,  $C_5H_4N \cdot OH$ , lately described by O. Fischer and E. Renouf (this vol., p. 1050). This shows that the product of the action of boiling strong sulphuric acid on piperidine contains  $\beta$ -pyridinemonosulphonate, but its presence

is probably due to the action of sulphuric acid on pyridine, small quantities of which are produced by the oxidation of some of the piperidine by the sulphuric acid at the high temperature of the reaction, and not by the direct action of the acid on piperidine.

The fusion of the sulphonates should be carried out with potash, as more bye-products are produced when soda is used, and the yield is not so good.

L. T. T.

**Derivatives of Hydroxypyridine from Pyridinesulphonic Acid.** By O. FISCHER and E. RENOUF (*Ber.*, 17, 1896—1899).—In a previous communication (this vol., p. 1050), the authors described the above  $\beta$ -hydroxypyridine. The melting point of the pure body is  $124.5^\circ$ . The *platinochloride* yields yellow needles easily soluble in water and alcohol; the *oxalate* soft yellowish needles melting at  $175^\circ$ , and easily soluble in water, sparingly in absolute alcohol; the *picrate* yellow needles, sparingly soluble in alcohol; the *methiodide* yellowish-white needles, easily soluble in water and alcohol, insoluble in ether; the *methochloride* colourless needles, which yield a *platinochloride* crystallising in orange-coloured needles.  $\beta$ -*Ethoxypyridine*, prepared by the action of ethyl bromide on the potassium-compound of hydroxypyridine, is a colourless oil, which is volatile in steam. It yields a *platinochloride* crystallising in prisms of melting point  $192^\circ$ . *Acetoxypyridine*,  $C_5H_5N.OAc$ , is obtained by boiling the hydroxy-compound with acetic anhydride. It is an almost colourless oil, boiling at  $210^\circ$  (uncorr.), and has a pleasant odour. It is easily soluble in acids and water, and the aqueous solution has a neutral reaction. The *hydrochloride* and *platinochloride* are both easily soluble in water and alcohol, the oxalate rather less so. *Dibromoxypyridine* is obtained by treating the hydroxy-compound with bromine-water. It forms soft colourless needles, easily soluble in water and alcohol, sparingly so in benzene. An aqueous solution gives a violet colour with ferric chloride. The *hydrobromide*, *hydrochloride*, *oxalate*, and *picrate*, are sparingly soluble; the *sulphate* and *platinochloride* easily soluble. Tin and hydrochloric acid act very slowly on  $\beta$ -hydroxypyridine, ammonia, and probably pyridine being formed; but the latter in such small quantity that the authors have not yet been able to conclusively prove its presence.

L. T. T.

**Derivatives of Orthhydroxyquinoline.** By O. FISCHER and E. RENOUF (*Ber.*, 17, 1642—1646).—The azo-compound,  $C_{15}H_{11}N_3SO_4$ , obtained from diazobenzenesulphonic acid and orthhydroxyquinoline is an orange dye forming magnificent crystalline alkali salts. On reducing the azo-compound with stannous chloride, and subsequently decomposing the yellow tin compound with sulphuretted hydrogen, amidohydroxyquinoline hydrochloride is formed, from which the base may be obtained by adding soda and extracting with ether. *Amidohydroxyquinoline* is somewhat unstable, but yields stable salts; the *sulphate*,  $C_9H_8N_2O.H_2SO_4$ , forms sparingly soluble silky needles; the *hydrochloride*,  $C_9H_8N_2O.2HCl$ , is very readily soluble. *Quinoline-quinone*,  $C_9H_5NO_2$ , is prepared by oxidising amidohydroxyquinoline sulphate with chromic mixture, and when purified by crystallisation

from benzene or alcohol forms soft flat needles having a peculiar green lustre. It decomposes at  $110-120^{\circ}$ . Its basic properties are but feeble, its salts being decomposed by water. Quinolinequinone is decomposed by soda, baryta-water, sodium carbonate solution, and even by barium carbonate. The *anilide of quinolinequinone*,  $C_{15}H_{10}N_2O_2$ , is prepared by boiling an alcoholic solution of the quinone with an excess of aniline. It is very similar to the corresponding naphthaquinone derivative obtained by Zincke (*Ber.*, **12**, 1644); it crystallises in small copper-coloured scales with green lustre, dyes deep copper-red, and yields violet solutions with cold dilute mineral acids; it seems to melt a little above  $190^{\circ}$ . *Quinolinequinol* is prepared by the action of sulphurous acid on an alcoholic solution of the quinone. It is moderately soluble in water, and crystallises from benzene in slender needles; it yields stable salts, the *sulphate* crystallising in soft orange-yellow needles, sparingly soluble in water, and decomposing when heated to about  $220^{\circ}$ ; the *hydrochloride* forms more readily soluble orange-coloured needles. Ferric chloride converts quinolinequinol into the quinone even in the cold.

With regard to the constitution of the above compounds, it is assumed from their analogy with the corresponding naphthol derivatives, that the side groups occupy similar positions, so that in amido-hydroxyquinoline the amido- and hydroxy-groups occupy the para-position in the benzene nucleus. That the substitution occurs only in the benzene nucleus is proved by the oxidation of amido-hydroxyquinoline to pyridinedicarboxylic acid.

Parahydroxyquinoline and metahydroxyquinoline also yield orange-coloured azo-dyes, and it is intended to prepare from these the derivatives corresponding with the above. A. K. M.

**Diquinoline from Benzidine.** By W. ROSER (*Ber.*, **17**, 1817—1820).—Employing Skraup's method (*Abstr.*, 1883, 85 and 92), the author heated a mixture of nitrobenzene and benzidine with glycerol and sulphuric acid. Dinitrodiphenyl may be used in place of nitrobenzene, and hydrazobenzene in place of benzidine.

*Diquinoline*,  $C_{18}H_{12}N_2$ , thus prepared, crystallises in small yellow plates which melt at  $178^{\circ}$ , and is easily soluble in boiling water and in benzene; sparingly in alcohol and ether. The *sulphate* crystallises in short needles; the *hydrochloride* in concentrically grouped needles; the *chromate* and *platinochloride* both form sparingly soluble yellow crystalline powders. Fuming nitric acid yields the sparingly soluble *nitrate*, but has no further action on the base even when heated with it. When bromine-water is added to a solution of the hydrochloride a *tetrabromo-addition product*,  $C_{18}H_{12}N_2Br_4$ , is formed, which on being boiled with water gives up bromine and regenerates diquinoline. A reduction product of diquinoline, obtained by boiling with tin and hydrochloric acid, could not be obtained in a crystalline form. A *disulphonic acid*,  $C_{18}H_{10}N_2(SO_3H)_2$ , is formed when the base is heated with fuming sulphuric acid at  $190^{\circ}$ . It is insoluble in water and alcohol, but dissolves in ammonia to form a characteristic *ammonium salt*, which crystallises in glittering, white, sparingly soluble needles.

The *potassium* and *sodium salts* are both very sparingly soluble, the

latter crystallising with 5 mols.  $\text{H}_2\text{O}$ . The *magnesium salt* is precipitated in the form of small needles when a mixture of solutions of the ammonium salt and of magnesium sulphate is heated. When fused with caustic potash, the disulphonic acid yields a very unstable *dihydroxydiquinoline*, which forms a red colouring matter with diazo-compounds. Diquinoline unites readily with the haloid salts of the alcohol radicles, forming easily crystallisable additive products. The *dimethiodide*,  $\text{C}_{18}\text{H}_{12}\text{N}_2(\text{MeI})_2$ , forms small yellow crystals which are easily soluble in water, sparingly so in alcohol, and melt with decomposition at  $300^\circ$ ; the *diethiodide* forms yellow needles soluble in water and melting with decomposition at  $270^\circ$ ; on oxidation with potassium pernauganate it yields a red substance of acid properties, which is now under investigation. Weidel's isomeric  $\alpha$ -diquinoline (Abstr., 1882, 69) forms only additive products with 1 mol. methyl iodide, &c. The metallic salts of  $\alpha$ -diquinoline are very unstable and are decomposed even by water; those of the present compound, on the other hand, are quite stable, so that, although resembling one another in many points (melting point, sulphonic acids, crystalline form, &c.), these two compounds are certainly not identical.

From the method of formation, the conjugation of the two quinoline nuclei in this compound must take place between the benzene-rings, whereas in Weidel's diquinoline it is probable (from analogy with the formation of dipyridine by the action of sodium on pyridine), that the conjugation takes place between the pyridine-rings.

L. T. T.

**Formation of Diquinoline by Aid of Heat.** By J. ZIMMERMANN and A. MÜLLER (*Ber.*, 17, 1965—1966).—By passing the vapour of quinoline through iron tubes heated to a dull red heat, the authors obtained a diquinoline,  $\text{C}_{18}\text{H}_{12}\text{N}_2$ , identical with the base described by Japp and Graham (*Trans.*, 1881, 174) as diquinolyline. A. J. G.

**Peculiar Method of Formation of Diquinoline.** By O. FISCHER and H. v. LOO (*Ber.*, 17, 1899—1902).—Orthoquinolinesulphonic acid when subjected to dry distillation yields  $\beta$ -diquinoline, identical with that described by Japp and Graham (*Trans.*, 1881, 174), and by Weidel (*Monatsh.*, 2, 501). The yield was 10 per cent. of the sulphonic acid employed. It sublimes in beautiful iridescent scales, and forms a characteristic sulphate,  $\text{C}_{18}\text{H}_{12}\text{N}_2\cdot\text{H}_2\text{SO}_4$ . The *hydrochloride* forms hard stellate clusters of needles; the picrate yellow needles sparingly soluble in benzene.

*Anuquinolinecarboxylic acid*,  $\text{C}_{10}\text{H}_7\text{NO}_2$ , is obtained by the oxidation of  $\beta$ -diquinoline with chromic acid. It crystallises in tufts of pale yellow needles; melts at  $255$ — $257^\circ$ , and decomposes into quinoline and carbonic anhydride at a few degrees higher. The *platinochloride* has the formula  $(\text{C}_{10}\text{H}_7\text{NO}_2)_2\cdot\text{H}_2\text{PtCl}_6$ . The *alkali salts* are easily soluble, the *copper*, *lead*, and *cadmium salts* are amorphous, the *calcium salt* yields silky needles. This acid is therefore different from all the six quinolinecarboxylic acids at present known.

The same diquinoline is also obtained, but in much smaller proportion, by the dry distillation of meta- and para-quinolinesulphonic acids.

L. T. T.



**Formation of Quinaldine.** By G. SCHULTZ (*Ber.*, **17**, 1965).—The author considers Döbner and Miller to be in error in supposing the solid bases obtained by them (*Ber.*, **17**, 1698) as bye-products in their method of preparing quinaldine, to be intermediate products in the formation of quinaldine, inasmuch as that they are not converted into quinaldine by boiling with hydrochloric acids. A. J. G.

**Quinaldine Bases.** By O. DOEBNER and W. v. MILLER (*Ber.*, **17**, 1698—1712).—In a previous paper (this vol., p. 183), the authors mentioned the formation of secondary products in the preparation of quinaldine; these are principally ethylaniline, boiling at 205°, and tetrahydroquinaldine, boiling at 246—248°. If aniline, paraldehyde and hydrochloric acid are allowed to react in the cold, very little quinaldine is produced, a mixture of amorphous bases being obtained which yields quinaldine when heated. The same product is obtained on warming an aqueous solution of aniline, paraldehyde, and hydrochloric acid.

Nitro-derivatives of quinaldine are prepared by dissolving quinaldine (100 grams) in the equivalent quantity of nitric acid, and adding the solution to a mixture of sulphuric (600 grams) and fuming nitric acids (600 grams). The product contains ortho- and meta-nitroquinaldine. *Ortho-nitroquinaldine*,  $C_{10}H_8N.NO_2$ , crystallises from dilute alcohol in long needles, melting at 137°; it dissolves readily in alcohol, ether, and benzene, sparingly in cold but more readily in hot water. The *hydrochloride*,  $C_{10}H_8N_2O_2.HCl$ , crystallises in large vitreous prisms which are decomposed by water with separation of the base; the *platinochloride*,  $(C_{10}H_8N_2O_2)_2.H_2PtCl_6$ , crystallises from hot concentrated hydrochloric acid in small needles. *Orthamidoquinaldine*,  $C_{10}H_{10}N_2$ , melts at 56°, is sparingly soluble in water, very readily in alcohol, ether, and hot light petroleum, and crystallises from the latter in long prisms; the *hydrochloride*,  $C_{10}H_{10}N_2.HCl$ , crystallises from alcohol in golden-yellow needles; the platinochloride is obtained as a yellow precipitate, which is decomposed on standing, more rapidly on warming. *Metanitroquinaldine*,  $C_{10}H_8N_2O_2$ , is much more readily soluble in dilute alcohol than the ortho-derivative, and crystallises in long slender needles melting at 82°; it is sparingly soluble in water, readily in ether and in acids. The *hydrochloride*,  $C_{10}H_8N_2O_2.HCl$ , crystallises in prisms, and dissolves readily in water without decomposition; the *platinochloride*,  $(C_{10}H_8N_2O_2)_2.H_2PtCl_6$ , crystallises in nodules or in needles. *Metamidoquinaldine*,  $C_{10}H_8N.NH_2$ , is readily soluble in hot water, alcohol, and benzene, sparingly in ether, more readily in light petroleum; the dry base has a greenish lustre, the ethereal solution a bluish-green fluorescence. It crystallises from water with 1 mol.  $H_2O$ , which it loses at 100°, and when anhydrous it melts at 104—105°. The hydrochloride,  $C_{10}H_{10}N_2.HCl$ , crystallises from alcohol in red curved needles, soluble in water with yellowish-red coloration.

By the action of fuming sulphuric acid on quinaldine, three sulphonic acids are produced, all of which probably contain the sulphonic group in the benzene nucleus. The chief product is named by the authors  *$\beta$ -quinaldinesulphonic acid*,  $C_{10}H_8N.SO_3H$ ; it is sparingly

soluble in cold, more readily in hot water, and crystallises in monoclinic prisms. The barium and silver salts are sparingly soluble, the sodium and potassium salts readily soluble. The other two acids are *ortho*- and *para*-quinaldinesulphonic acids. The *ortho*- acid is more readily soluble in cold water than the  $\beta$ -acid, and is readily soluble in hot water; it crystallises in long, flat, triclinic prisms. When fused with potash, it yields orthhydroxyquinaldine, melting at 74°. *Para*-quinaldinesulphonic acid is distinguished from its isomerides by its greater solubility in water. It is much more advantageously prepared by heating sulphanilic acid (100 grams), with paraldehyde (80 grams), and hydrochloric acid (100 grams). It forms small monoclinic crystals, and yields parahydroxyquinaldine, melting at 213°, on fusion with potash.

*Orthohydroxyquinaldine*,  $\text{OH.C}_6\text{H}_3\langle \begin{smallmatrix} \text{N : CMe} \\ \text{CH : CH} \end{smallmatrix} \rangle$ , may also be obtained by heating orthamidophenol hydrochloride (200 grams) with paraldehyde (200 grams) and crude concentrated hydrochloric acid (150 grams); the product is diluted with water, filtered, saturated with sodium carbonate, and steam-distilled. It crystallises from dilute alcohol in colourless prisms, melts at 74°, and boils at 266—267°; it is sparingly soluble in water, readily in benzene, ether, and hot alcohol. It forms salts with bases and with acids, but is insoluble in alkaline carbonates; the hydrochloride, nitrate, and sulphate are readily soluble; the *platinochloride*,  $(\text{C}_{10}\text{H}_9\text{NO})_2, \text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}$ , crystallises in clusters of yellow needles, sparingly soluble in cold water.

*Tetrahydrorthohydroxyquinaldine*,  $\text{C}_{10}\text{H}_{12}\text{N.OH}$ , obtained by the action of tin and hydrochloric acid on hydroxyquinaldine, is a liquid boiling at 278—282°. Benzoic and acetic chlorides react energetically with orthohydroxyquinaldine, yielding benzoic and acetic derivatives. The *methyl-derivative*,  $\text{C}_{10}\text{H}_9\text{N.OMe}$ , may be obtained from methyl iodide and hydroxyquinaldine, but more advantageously by heating a mixture of orthanisidine (2 parts), hydrochloric acid (4 parts), and paraldehyde (3 parts). It melts at 125°, boils at 282°, is sparingly soluble in water, readily in alcohol, ether, and hot benzene. The hydrochloride, sulphate, and nitrate are readily soluble; the chromate crystallises in long orange-red needles, sparingly soluble in cold water; the *platinochloride*,  $(\text{C}_{11}\text{H}_{11}\text{NO})_2, \text{H}_2\text{PtCl}_6$ , forms sparingly soluble yellow needles. *Tetrahydrorthomethoxyquinaldine*,  $\text{C}_{10}\text{H}_{12}\text{N.OMe}$ , boils at 270°, is sparingly soluble in water, readily in alcohol and ether; its salts give a magenta coloration with ferric chloride; a nitroso-derivative can be obtained. The hydrochloride,  $\text{C}_{10}\text{H}_{12}\text{N.OMe.HCl}$ , is readily soluble in water, and sublimes at about 150° in stellate crystals. On heating the hydro-base with methyl iodide at 100°, the tertiary base,  $\text{C}_{10}\text{H}_{11}\text{MeN.OMe}$ , is produced; this boils at 260—262°, yields a soluble hydrochloride, and furnishes a green dye when heated with benzotrichloride and zinc chloride. The *platinochloride*,  $(\text{C}_{12}\text{H}_{17}\text{NO})_2, \text{H}_2\text{PtCl}_6$ , forms stellate clusters of yellow needles.

*Parahydroxyquinaldine* may be obtained, in the same way as the isomeric *ortho*-compound, from paraquinaldinesulphonic acid, and from paramidophenol, aldehyde, and hydrochloric acid. It is not volatile in steam, but may be distilled with very slight decomposition;

it forms spear-shaped crystals, melts at  $213^{\circ}$ , dissolves very sparingly in cold water, readily in alcohol and ether, and is also soluble in acids and alkalis. The *platinochloride*,  $(C_{10}H_9NO)_2 \cdot H_2PtCl_6 + 2H_2O$ , forms stellate clusters of yellow needles.  $\beta$ -*Hydroxyquinaldine*,  $C_{10}H_9N \cdot OH$ , obtained from  $\beta$ -quinaldinesulphonic acid, crystallises in colourless silvery scales, softens at about  $220^{\circ}$ , melts at  $232$ – $234^{\circ}$ , and can be distilled with slight decomposition; it is almost insoluble in boiling water, sparingly in cold but more readily in hot alcohol, readily in ether. The sulphate and *hydrochloride*,  $C_{10}H_9NO \cdot HCl + 2H_2O$ , crystallises in long lemon-yellow needles, sparingly soluble in cold water; the *platinochloride*,  $(C_{10}H_9NO)_2 \cdot H_2PtCl_6 + 2H_2O$ , also forms yellow needles.  $\beta$ -Hydroxyquinaldine is soluble in dilute alkalis, but insoluble in alkaline carbonates; it is distinct from the  $\gamma$ -compound obtained by Knorr (this vol., p. 335), and probably contains the hydroxyl-group in the meta-position.

*Trimethylquinaldine*,  $C_{10}H_6NMe_3$ , prepared from crystallised cumidine (Abstr., 1883, 324), paraldehyde and hydrochloric acid, is an oil boiling at  $297$ – $300^{\circ}$ , and solidifying at  $20^{\circ}$ ; it is insoluble in water, readily soluble in alcohol and ether. The *chromate*,  $(C_{13}H_{15}N)_2 \cdot H_2Cr_2O_7$ , crystallises in long golden-yellow needles.  $\alpha$ -*Naphthaquinaldine*,  $C_{10}H_6 \begin{smallmatrix} N : CMe \\ CH : CH \end{smallmatrix}$ , is prepared by heating  $\alpha$ -naphthylamine (1 part), with paraldehyde (1 part), and hydrochloric acid (2 parts), at  $100$ – $110^{\circ}$ . It is a heavy liquid, boiling above  $300^{\circ}$ ; the hydrochloride, nitrate, and sulphate are readily soluble in water, and in very dilute solution exhibit blue fluorescence. The *platinochloride*,  $(C_{14}H_{11}N)_2 \cdot H_2PtCl_6 + 2H_2O$ , crystallises in concentrically grouped needles; the *chromate*,  $(C_{14}H_{11}N)_2 \cdot H_2Cr_2O_7$ , forms yellow crystals.  $\beta$ -*Naphthaquinaldine* forms large colourless needles, melts at  $82^{\circ}$ , and boils above  $300^{\circ}$ ; it dissolves sparingly in water, readily in alcohol and ether. The *platinochloride*,  $(C_{14}H_{11}N)_2 \cdot H_2PtCl_6 + 2H_2O$ , and the *chromate*,  $(C_{14}H_{11}N)_2 \cdot H_2Cr_2O_7$ , both form yellow sparingly soluble needles.

A. K. M.

**Homologues of Quinaldine.** By O. DOEBNER and W. V. MILLER (*Ber.*, 17, 1712–1721).—The method previously given for the preparation of quinaldine (this vol., p. 183) may be employed for the production of its homologues, provided the aldehydes used contain primary alcohol radicals, that is,  $CH_2R \cdot CHO$ . From propaldehyde, aniline, and hydrochloric acid, a base,  $C_{12}H_{13}N$ , is obtained which melts at  $56^{\circ}$ , boils at  $268$ – $269^{\circ}$  (bar. = 711 mm.), and has the characteristic odour of quinaldine; it is sparingly soluble in water, readily in alcohol, benzene, and ether, and crystallises from the last solvent in large well-formed monoclinic prisms. The sulphate and hydrochloride crystallise from alcohol in small prisms extremely soluble in water. The *platinochloride*,  $(C_{12}H_{13}N)_2 \cdot H_2PtCl_6$ , crystallises in bright-yellow needles, the *picrate*,  $C_{12}H_{13}N \cdot C_6H_3N_3O_7$ , in yellow crystals, and the *chromate*,  $(C_{12}H_{13}N)_2 \cdot H_2Cr_2O_7$ , in small yellowish-brown prisms. The *methiodide*,  $C_{12}H_{13}N \cdot MeI$ , forms lemon-yellow needles very readily soluble in hot water or hot alcohol, but insoluble in ether; it melts at  $196^{\circ}$  with partial decomposition. On oxidising the base  $C_{12}H_{13}N$  with chromic

acid dissolved in sulphuric acid, an acid,  $C_{11}H_9NO_2$ , is formed melting at  $140^\circ$  and yielding a sparingly soluble *copper salt*,  $(C_{11}H_9NO_2)_2Cu$ . When heated with soda-lime, this acid furnishes a methylquinoline boiling at about  $250^\circ$  (i.e., higher than quinaldine) and the *platinochloride* of which crystallises in orange-yellow needles of the composition  $(C_{10}H_9N)_2, H_2PtCl_6 + 2H_2O$ . This is no doubt  $\beta$ -methylquinoline,  $C_6H_4<\begin{smallmatrix} N:CH- \\ CH: CMe \end{smallmatrix}>$ , and therefore the acid must be regarded as a

*methylquinolinecarboxylic acid*, and the base  $C_{12}H_{13}N$  as an *ethylmethylquinoline*. The formation of the latter from propaldehyde being analogous to that of quinaldine from acetaldehyde, it is extremely probable that an intermediate product, ethylmethylacrolein,  $CHEt: CMe.CO.H$ , is first formed, and then unites with aniline to form  $\alpha$ -ethyl- $\beta$ -methylquinoline,  $C_6H_4<\begin{smallmatrix} N:CEt- \\ CH: CMe \end{smallmatrix}>$ . The constitu-

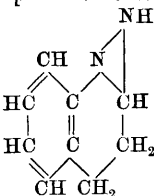
tion of the acid  $C_{11}H_9NO_2$  must then be  $C_6H_4<\begin{smallmatrix} N:C(COOH) \\ CH: CMe \end{smallmatrix}>$ .

The reduction of ethylmethylquinoline takes place less readily than is the case with quinaldine; the *hydrogenated base*,  $C_{12}H_{17}N$ , obtained is a colourless liquid of agreeable odour, boiling at  $260$ — $262^\circ$ ; it gives a red coloration with ferric chloride, and combines with nitrous acid to a yellowish-red nitroso-compound. The *platinochloride* is a bright yellow crystalline precipitate; the hydrochloride is sparingly soluble (distinction from ethylmethylquinoline), and crystallises in tufts of needles. *Propylaniline*,  $NHPhPr$ , and the above hydrobase are obtained as secondary products in the preparation of ethylmethylquinoline. Propylaniline boils at  $214$ — $216^\circ$ , and yields a crystalline nitroso-derivative, the *platinochloride* of which crystallises in long concentric prisms. *Propylethylquinoline*,  $C_{14}H_{17}N$ , obtained from normal butaldehyde, aniline, and hydrochloric acid, boils at  $290^\circ$  and yields a crystalline picrate. *Butylpropylquinoline*,  $C_{16}H_{21}N$ , prepared from isovaleraldehyde,  $CHMe_2.CH_2.CHO$ , and aniline, forms a bright yellow oil, boils at  $293$ — $294^\circ$ , and yields crystalline salts; the *nitrate* is almost insoluble in cold water, the *hydrochloride* and *sulphate* are readily soluble; the *platinochloride*,  $(C_{16}H_{21}N)_2, H_2PtCl_6$ , forms sparingly soluble yellow prisms, and the picrate,  $C_{16}H_{21}N, C_6H_3N_3O_7$ , large yellow plates. *Hexylamylquinoline*,  $C_{20}H_{29}N$ , obtained from cœnanthaldehyde and aniline, is a colourless oil boiling between  $320^\circ$  and  $360^\circ$ . It is not dissolved by concentrated hydrochloric acid, but is soluble in concentrated sulphuric and nitric acids, the addition of water, however, reprecipitates it from these solutions. The sulphate separates from its alcoholic solution in needles or wart-like crystals; the *picrate*,  $C_{20}H_{29}N, C_6H_2(NO_2)_3.OH$ , crystallises in yellow needles, sparingly soluble in water and cold alcohol; the *platinochloride*,  $(C_{20}H_{29}N)_2, H_2PtCl_6$ , forms large yellow plates. The *hydrogenated base*,  $C_{20}H_{33}N$ , is obtained as a secondary product; it yields no crystalline picrate and no *platinochloride*.

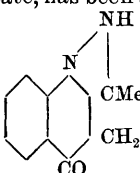
The resemblance which the above bases show in their chemical behaviour indicates that they have a similar constitution, their general formula being accordingly  $C_6H_4<\begin{smallmatrix} N:C(CH_2R) \\ CH: CR \end{smallmatrix}>$ . A table is ap-

pended showing the formulæ 1, of the aldehydes experimented on; 2, of the hypothetical intermediate alkylacroleins; and 3, of the quinaldine-bases formed from them. A. K. M.

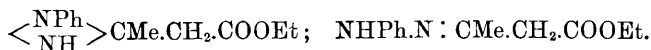
**Constitution of Quinizine-derivatives (III).** By L. KNORR (*Ber.*, 17, 2032—2049).—The author applies the term quinizine-derivatives to a new class of compounds derived from a hypothetical

base, *quinizine*, of the formula , of which the first

representative methoxyquinizine formed by condensation from phenylhydrazine and ethyl acetoacetate, has been already described (this

vol., pp. 302, 1153); the formula  then assigned to it is

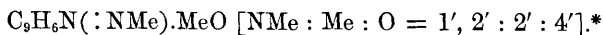
further confirmed by the following considerations. The formation of this body occurs in two stages. The intermediate compound, ethyl phenylhydrazineacetoacetate, formed in the cold with elimination of water, must be represented by either one of the formulæ



The dimethoxyquinizine formed by replacing the hydrogen-atom attached to nitrogen by methyl does not yield methylaniline when decomposed either by heating with hydrochloric acid at 200° or by distillation with zinc-dust. Secondary hydrazines do not yield the corresponding alkyl quinizines by condensation with ethyl acetoacetate. These facts render the second formula improbable. In the second stage of the reaction, at 100°, ethyl phenylhydrazineacetoacetate suffers further condensation with elimination of alcohol; without doubt, here the ethoxy-group combines with a hydrogen-atom from the benzene-ring, and not with one from the neighbouring methylene-group, it being found in methoxyquinoline that the latter must remain intact, as the isonitrosomethoxyquinoline obtained by the action of nitrous acid on the base is identical with that obtained by direct condensation from phenylhydrazine and ethyl isonitrosoacetoacetate. The chemical behaviour of methoxyquinoline is in complete accordance with this formula. It is at once acid and base, the acid properties disappearing on substitution of alcohol radicles for the hydrogen of the imido-group. The methylene-group is no longer capable of having its hydrogen replaced by metals, but otherwise

shows the greatest resemblance in behaviour to that possessed by it in acetoacetates.

*Dimethyloxyquinizine (antipyrine).*



This compound has been already shortly described (*loc. cit.*). It is distinguished from its isomerides by containing the second methyl in the imido-group. Under the name of antipyrine it is now used extensively in Germany as a febrifuge.

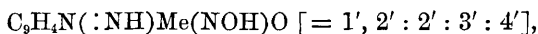
*Isonitrosoantipyrine*,  $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_2$ , is prepared by the action of nitrous acid on a solution of antipyrine. It forms green crystals, explodes when heated at  $200^\circ$ , is insoluble in water and dilute acids, soluble in alkalis and acetic acid, moderately soluble in alcohol, sparingly soluble in chloroform and ether. By reduction with zinc and acetic acid, it is converted into an oily base that has not been further investigated.

*Nitroantipyrine*,  $\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}\cdot\text{NO}_2$  [ $\text{NO}_2 = 3'$ ], is obtained by gently heating a solution of antipyrine in concentrated nitric acid or by the action of nitric acid on isonitrosoantipyrine. It crystallises in white needles, melts at  $270-280^\circ$ , is insoluble in water and alkalis, sparingly soluble in strong nitric and hydrochloric acids, from which it is reprecipitated unchanged on addition of water.

*Benzylidineantipyrine* is obtained as hydrochloride by the action of concentrated hydrochloric acid on a solution of antipyrine in benzaldehyde. It has the formula  $\text{C}_{29}\text{H}_{28}\text{N}_4\text{O}_2 = \text{CHPh}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{O})_2$ , the benzylidine being most likely united to the antipyrine-groups at the [3'] positions as the compound does not react with nitrous acid. The free base forms lustrous crystals and melts at  $201^\circ$ . The hydrochloride crystallises in long, interlaced, silky needles.

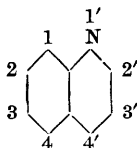
By heating antipyrine with hydrochloric acid at  $200^\circ$ , it suffers complete decomposition, yielding, amongst other products, much aniline and small quantities of methylamine. By distillation with zinc-dust, antipyrine yields benzene, aniline, a base boiling at  $86-87^\circ$  (still under investigation), and other products.

*Isonitrosomethyloxyquinizine,*



is obtained by the action of nitrous acid on methyloxyquinizine or by direct condensation from phenylhydrazine and ethyl isonitrosoacetoacetate. It crystallises in orange-yellow needles, melts at  $137^\circ$ ,

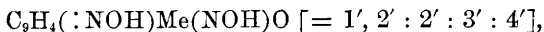
\* In the notation of the quinoline series, 1. 2. 3. 4 refer to the positions in the benzene-ring, and 1'. 2'. 3'. 4' to the corresponding positions in the basic ring containing the nitrogen, where N = 1', as shown in the annexed symbol:—



In the quinizines where the :NH or other similar group is united to both 1' and 2', the constitutional formula is written :NH = 1', 2', &c.—C. E. G.

slowly sublimates below  $100^{\circ}$ , and is decomposed when heated above the melting point. It is sparingly soluble in water and acids, readily in hot glacial acetic acid and alcohol, moderately in ether. It is a strong acid, dissolves in alkalis with yellowish-red coloration, and yields a yellow crystalline sodium salt.

*Isonitrosomethyldioxyquinizine*,

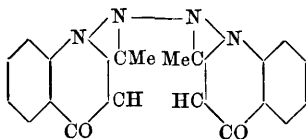


is prepared by mixing an alkaline solution of methyloxyquinizine with excess of sodium nitrite and pouring the mixture into dilute sulphuric acid. It crystallises in brilliant prisms, melts at  $135^{\circ}$ , is soluble in alcohol and ether, insoluble in acids, soluble in alkalis to a yellow liquid. Nitric acid readily converts both this and the preceding compound into a blue compound, most probably identical with diquinizine-blue.

By the action of nitric acid on methyloxyquinizine, an oil can be obtained which is probably methyldioxyquinizine; it is very readily oxidised to di-quinizine-blue, and is converted into nitrosomethyldioxyquinizine by the action of nitrous acid. It could not be obtained in a pure state.

*Di-methyloxyquinizine*,  $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_2$ , is formed by heating a mixture of methyloxyquinizine and phenylhydrazine to boiling. As it is also formed by condensation from ethyl diacetosuccinate and phenylhydrazine (p. 1382), it must be regarded as formed by the union of 2 mols. of methyloxyquinizine with elimination of 2 atoms of hydrogen, the position of union being  $[3' : 3']$ . It crystallises in rhombic forms, is insoluble in nearly all solvents, except alkalis, and has both acid and basic properties. Heated with methyl iodide and methyl alcohol, it yields *diantipyrine*,  $\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_2$ , melting at  $250^{\circ}$ . The corresponding ethyl compound,  $\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_2$ , melts at  $240\text{--}250^{\circ}$ . These bases are distinguished from antipyrine by their sparing solubility in water.

*Diquinizine-blue*,  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_2$ , is obtained as already mentioned by oxidation of many of the quinizine-derivatives: it is best prepared by mixing di-methyloxyquinizine in alkaline solution, with excess of sodium nitrite solution, and pouring the mixture into dilute sulphuric acid, when it separates in flocks which can be crystallised from chloroform. It forms blue needles, is insoluble in water, dilute acids, and dilute alkalis, sparingly soluble in alcohol and ether. It dissolves in chloroform and concentrated sulphuric acid, the solutions having an indigo-blue colour, and giving a spectrum similar to that of indigo. It does not dye fibres. It is decomposed on boiling it with strong alkali or acids, and is decolorised by chlorine and nitric acid. Reducing agents convert it into di-methyloxyquinizine. The author assigns to it the constitution



A. J. G.

**Action of Substituted Acetoacetates on Phenylhydrazine.**

By L. KNORR and A. BLANK (*Ber.*, **17**, 2049—2052).—These quinizine-derivatives are prepared in similar manner to that described for methyloxyquinizine (this vol., p. 302).

2'. 3'-Dimethyloxyquinizine,  $C_9H_5N(:NH)Me_2O$  [Me: Me = 2': 3'], prepared from phenylhydrazine and ethylic methylacetoacetate, forms a crystalline powder and melts at 127—132°. It is isomeric with antipyrène. Heated with methyl iodide and methyl alcohol, it yields a base melting at 84°, and analogous to antipyrène. A diquinizine is not formed by heating it with excess of phenylhydrazine. Oxidising agents, best nitrous acid, convert it into azodimethyloxyquinizine,  $C_9H_5NMe_2O:N:N:C_9H_5NMe_2O$ , which crystallises in long needles, melts at 164°, is soluble in alcohol and glacial acetic acid, insoluble in water, acids, and alkalis.

2'. 3'-Methylethyloxyquinizine,  $C_9H_5N(:NH)MeEtO$ , prepared from phenylhydrazine and ethylic ethylacetoacetate, crystallises in needles with 1 mol.  $H_2O$ , melts when anhydrous at 108°, is readily soluble in chloroform, alcohol, benzene, and hot water, less soluble in ether and light petroleum. By the action of oxidising agents, it is converted into azoethylmethyloxyquinizine,  $C_{24}H_{26}N_2O_4$ , melting at 160°.

The action of ethylic acetosuccinate on phenylhydrazine unassisted by heat gives rise to ethylic phenylizinetosuccinate,  $C_{16}N_{22}N_2O_4$  (m. p. 80°), which by heating at 150° is converted into alcohol and ethylic methyloxyquinizinetosuccinate,  $C_{14}H_{16}N_2O_3$ , forming crystals melting at 138°. It is saponified by heating with sulphuric acid, and yields the free acid. *Methyloxyquinizinetosuccinic acid*,



thus obtained, crystallises in needles, and melts at 178°.

A. J. G.

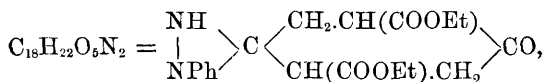
**Action of Ethylic Succinosuccinate on Phenylhydrazine.**

By L. KNORR and C. BÜLOW (*Ber.*, **17**, 2053—2057).—Knorr has described (this vol., p. 1154) a yellow substance of the formula



diquinizinehydrobenzene, which forms the main product of the action of ethylic succinosuccinate on phenylhydrazine. By working under varied conditions, the authors have now succeeded in obtaining by this reaction nearly all the substances whose formation could be theoretically predicted.

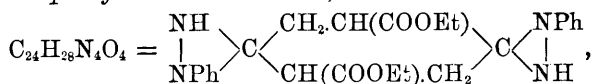
*Ethylic phenylizine succinosuccinate*,



is prepared by heating on the water-bath an excess of ethylic succinosuccinate with Fischer's phenylhydrazine reagent. It is only formed in small quantity, diquinizinehydrobenzene being the main product. It crystallises in interlaced needles, melts at 159—160°, is soluble in alcohol, insoluble in water, and has basic properties.

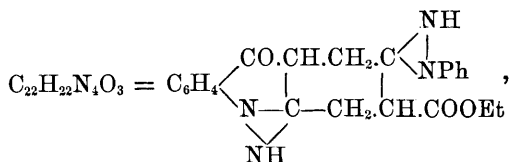


*Ethyl dicphenylizinsuccinosuccinate,*



is obtained amongst other products by heating for some hours a solution of phenylhydrazine (2 eq.) with ethylic succinosuccinate (1 eq.) in presence of acetic acid. It forms a yellow crystalline powder, melts at 205–206°, gives off a green vapour on heating, and dissolves in acids with a beautiful carmine-red coloration. It is decomposed by boiling with strong acids, without separation of phenylhydrazine, and does not yield a colouring matter on treatment with nitrous acid.

*Ethyl phenyliziquinizinhydrobenzenecarboxylate,*



is formed at the same time as the last substance, and can be separated by boiling with toluene, in which it is soluble. It crystallises in yellow needles, melts at 211–212°, is insoluble in water and alcohol, soluble in alkalis with yellow coloration, in acids with pale-rose coloration. By oxidation with nitrous acid or exposure to air its acid solution acquires an emerald-green tint, which by further oxidation turns dirty green. It gives off a green vapour when heated.

*Dimethyldiquinizinhydrobenzene*,  $\text{C}_{22}\text{H}_{25}\text{N}_4\text{O}_2$ , prepared by heating the sodium salt with methyl iodide, crystallises in yellowish needles, is soluble in chloroform and toluene, the solutions showing a fluorescence resembling that of uranium glass; it is but sparingly soluble or insoluble in most other solvents. The corresponding diethyl-compound resembles the foregoing in both preparation and properties.

By the action of nitrous acid on an alkaline solution of diquinizinhydrobenzene, a blue colouring matter of the formula  $\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}_2$  is obtained; when heated, it gives off purple-red vapours, and in part sublimes undecomposed. The same vapours and sublimate are obtained by heating diquinizinhydrobenzene.

A. J. G.

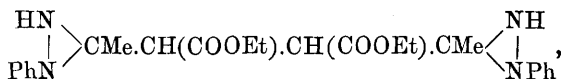
#### Action of Ethylic Diacetosuccinate on Phenylhydrazine.

By L. KNORR and C. BÜLOW (*Ber.*, 17, 2057–2060).—*Ethyl phenylizindiacetosuccinate*,  $\begin{array}{c} \text{HN} \\ | \\ \text{C} \\ | \\ \text{PhN} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{CMe}\cdot\text{CH}(\text{COOEt})\cdot\text{CH}(\text{COOEt})\cdot\text{CMe}$ , is

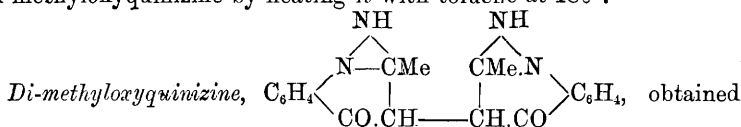
obtained by heating equal parts of phenylhydrazine and ethyl diacetosuccinate at 180°, and is separated from the di-methyloxyquinizine formed at the same time by boiling with alcohol, in which the latter is insoluble. It forms large crystals, melts at 91°, is

insoluble in alcohol, light petroleum, and glacial acetic acid, and insoluble in water.

*Ethyl diphenylizindiacetosuccinate*,



is best prepared by heating equal parts of phenylhydrazine and ethyl diacetosuccinate on the water-bath. It crystallises in lance-like forms, is insoluble in water, alcohol, acids, and alkalis, and is converted into di-methyloxyquinizine by heating it with toluene at  $180^\circ$ .



as above mentioned, is identical with the di-methyloxyquinizine prepared by heating methyloxyquinizine with phenylhydrazine (p. 1379). A solution of the sodium salt gives white precipitates with silver, lead, mercury, and nickel salts, a deep-blue precipitate with copper salts, a brownish-red precipitate with uranium salts, a blackish-brown precipitate with ferric salts, and a steel-blue precipitate with ferrous salts.

A. J. G.

**Cystine and Cysteine.** By E. BAUMANN (*Zeit. Physiol. Chem.*, **8**, 299—305).—If tin foil is added to a hydrochloric acid solution of cystine, there is at first no disengagement of gas, the levorotatory power also gradually diminishes until it reaches a point where no further change takes place. Only a minimal quantity of sulphuretted hydrogen is formed, which is not in accordance with the statements of Dewar and Gamgee. The hydrochloride of the new base cysteine is obtained by evaporating the filtrate, after removal of the tin by sulphuretted hydrogen. The base itself can be best prepared by carefully neutralising the alcoholic solution of the hydrochloride, washing with alcohol, and drying in a vacuum. It differs from cystine, being soluble in water, ammonia, acetic and mineral acids, and forms a fine indigo-blue colour with ferric chloride, which rapidly vanishes, cystine being precipitated; this is also true of the hydrochloride, although the colour is much weaker. When treated with potash, it furnishes the same decomposition-products as cystine, and is also very readily oxidised, cystine being the product formed. The author has assigned to it the formula  $\text{C}_3\text{H}_7\text{NSO}_2$ ; cystine being  $\text{C}_6\text{H}_{12}\text{N}_2\text{S}_2\text{O}_4$ .

Concentrated hydriodic acid fails to form thiolactic acid as expected, by the displacement of  $\text{NH}_2$  by H.

J. P. L.

**Cinchona Alkaloids.** By W. J. COMSTOCK and W. KÖNIGS (*Ber.*, **17**, 1984—1996).—In earlier communications (*Abstr.*, 1880, 673, 1882, 224), Königs has shown that cinchonine when treated with phosphoric chloride and oxychloride is converted into cinchonine chloride, from which by boiling with alcoholic potash a non-

oxygenated base, cinchine,  $C_{19}H_{20}N_4$ , is obtained; and that this when heated with concentrated hydrochloric acid at  $220-230^\circ$  is converted into apocinchine,  $C_{18}H_{17}NO$ , with separation of methyl chloride and ammonia.

*Cinchonidine chloride*,  $C_{19}H_{21}N_2OCl$ , is prepared by the action of phosphoric chloride and oxychloride on cinchonidine hydrochloride; it crystallises well, and melts at  $108-109^\circ$ . Heated with alcoholic potash it yields cinchine.

*Quinine chloride*,  $C_{20}H_{23}N_2OCl$ , is prepared by dissolving quinine hydrochloride (3 parts) in chloroform, and adding the liquid to finely powdered phosphoric chloride covered with chloroform; the mixture is heated for some time, then cooled in water, the chloroform decanted off, and the aqueous solution precipitated with ammonia. The base may be crystallised by adding ether to its solution in benzene; it forms colourless crystals, melts at  $151^\circ$ , and gives a green coloration with chlorine-water and ammonia, the coloration being much less intense than that obtained with quinine. Its solution in dilute sulphuric acid is not fluorescent.

*Chinine*,  $C_{20}H_{22}N_2O$ , prepared by the action of alcoholic potash on quinine chloride, forms colourless crystals containing 2 mols.  $H_2O$ , and melting at  $81-82^\circ$ ; it is soluble in water, ether, and light petroleum. The sulphate is readily soluble, and of neutral reaction. The solution in dilute sulphuric acid shows decided fluorescence, of a greener tint than that of quinine.

*Oxidation-products of Cinchine, Cinchonine, and Quinine.*—It has been shown that on oxidation with chromic acid cinchonine yields, together with carbonic anhydride and a little formic acid, a quinoline-carboxylic acid—cinchonic acid—(Königs, Abstr., 1879, 471; Skraup, *ibid.*, 656), and that quinine yields a methoxyquinolinecarboxylic acid—quinic acid—(Skraup, Abstr., 1879, 809), but of the bye-products little is known except that Weidel and Hazura obtained a small quantity of nitrohydroxyquinoline from the mother-liquors of cinchonic acid, by boiling them with nitric acid; and on distilling them with zinc-dust small quantities of  $\beta$ -ethylpyridine, quinoline, and a very little pyridine were formed (Abstr., 1883, 222).

In the authors' experiments, after removal of the cinchonic or quinic acid from the oxidation products, bromine-water is added, when from cinchonine and cinchine they obtained the insoluble tribromoxylepidine, and a soluble bromine-compound of the formula  $C_9H_{13}Br_2NO$ . In the case of quinine, the latter compound alone is obtained. *Tribromoxylepidine*,  $C_{10}H_6Br_3ON$ , can be crystallised from boiling alcohol; it does not melt at  $280^\circ$ , but can be sublimed in small quantity. It is sparingly soluble in boiling alcohol, chloroform, or benzene, more readily in hot acetic acid, insoluble in water, scarcely soluble in ammonia, sparingly in boiling aqueous soda; when it is boiled with sodium-amalgam and water, quinoline and hydroquinoline are formed in small quantity. Hydriodic acid converts it, in small part, into quinoline or lepidine. The soluble bromine-compound,  $C_9H_{13}Br_2NO + \frac{1}{2}H_2O$ , crystallises in colourless prisms, melts with decomposition at  $250^\circ$ , is very readily soluble in hot water, sparingly soluble in boiling alcohol, nearly or quite insoluble in

chloroform, benzene, and ether. The aqueous solution has an acid reaction, gives a precipitate with phosphotungstic acid, a resinous precipitate with potassium mercuric iodide, soluble in excess, and with gold chloride, a resinous precipitate that can be crystallised in flat ruby-red needles. Silver nitrate added to a hot aqueous solution precipitates half the bromine, a compound being formed whose aurochloride crystallises in clear yellow needles of the formula



Long boiling with excess of silver nitrate removes nearly the whole of the bromine. Dibromocinchonine was submitted to oxidation, to see if these bromo-derivatives would be formed, but the products were found to be cinchonic and hydrobromic acids. By boiling it with alcoholic potash, a base free from bromine (a dihydrocinchonine,  $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}^?$ ) was obtained; this crystallises in needles, melts at  $202\text{--}203^\circ$ , sublimes without decomposition, and is readily soluble in alcohol.

A. J. G.

**Quinine and Homoquinine.** By O. HESSE (*Annalen*, **225**, 95—108).—The author at the outset claims for himself the first notice of the presence in the bark of the *China cuprea* of an alkaloid which, if not identical with, at least closely resembles quinine. To this substance the name homoquinine has been given (comp. Howard, *Trans.*, 1882, 67). Objection is raised to Howard's statement that plants in the course of their growth are capable of the mutual conversion of quinine and cinchonidine, for all experiments in this direction have failed, so that the formation of quinine and cinchonidine must be considered to be independent phenomena.

Homoquinine is best obtained by dissolving the crude alkaloid in dilute sulphuric acid, reprecipitating by ammonia, then shaking up with ether, from which homoquinine separates out in the crystalline form. On repeating this process twice, the alkaloid is obtained practically pure. In a former paper the author assigned to homoquinine the formula  $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$  (*Abstr.*, 1883, 601; *Ber.*, **15**, 857); the numbers obtained in more recent analyses are best in accordance with a formula  $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$ . Homoquinine crystallises in concentrically grouped needles, belonging to the rhombic system, containing between 2 and  $2\frac{1}{2}$  mols.  $\text{H}_2\text{O}$ ; on exposure to the air they gradually deliquesce, but may be heated to  $100^\circ$  without melting. Homoquinine is less soluble in ether than quinine; it is readily soluble in alcohol, the solution having a strongly alkaline reaction and an intensely bitter taste. With acids, the alkaloid forms both neutral and acid salts, which differ from the corresponding salts of quinine by their greater solubility. The *neutral hydrochloride* forms an amorphous powder, the *acid hydrochloride* colourless prisms; the *platinochloride* crystallises in small orange-red prisms, the *neutral sulphate* in short six-sided colourless prisms; the thiocyanate is an amorphous powder.

In the specific rotatory power of the sulphate (1.25 grams dissolved in 10 c.c. normal hydrochloric acid and 25 c.c. water), ( $t = 15$ ,  $l = 220$ )  $[\alpha]_D = -235.6$ , due allowance being made for the proportion of water contained in the crystalline salt; this value is practically

identical with that of quinine sulphate. The neutral tartrate crystallises in tufts of needles containing 2 mols.  $H_2O$ .

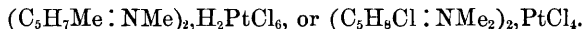
It was found possible to convert homoquinine into quinine by dissolving the alkaloid in hydrochloric acid, precipitating with soda, shaking up with ether, and adding sulphuric acid. On frequent repetition of the process, homoquinine is converted entirely into quinine sulphate. This result explains how homoquinine for some time eluded the observation of chemists. A few remarks are also added on the formation, under certain conditions, from quinine of an anhydride which behaves as a definite alkaloid, but can be reconverted into quinine, so that it would appear most probable that there exist several modifications of quinine, of which one is homoquinine.

V. H. V.

**Bromo-derivatives of Dimethylpiperidine.** By G. MERLING (*Ber.*, 17, 2139—2143).—*Bromodimethylpiperidineammonium bromide*,  $NMe_2(C_5H_9Br)''Br$ , is obtained together with dimethylpiperidine dibromide hydrobromide by the action of bromine on dimethylpiperidine, both dissolved in carbon bisulphide. The separation of the two products is effected by treatment with hot absolute alcohol, in which the former is very sparingly, the latter compound readily soluble. The ammonium bromide, which is formed in much the largest quantity, forms groups of colourless crystals, is readily soluble in water, but only very sparingly in alcohol, insoluble in ether. It is not decomposed by aqueous potash. By treatment with silver chloride and addition of platinic chloride, an orange-yellow platinochloride,  $(C_5H_9Br:NMe_2Cl)_2, PtCl_4$ , is precipitated. By digesting the aqueous solution with moist silver oxide ( $\frac{1}{2}$  mol. proportion) a liquid of strongly alkaline reaction is obtained, probably due to the formation of the hydroxide,  $C_5H_9Br:NMe_2.OH$ . This solution slowly loses its alkaline reaction when evaporated in a vacuum, the change taking place rapidly on heating. This change is due to an intermolecular action in which a new bromide of the formula



or  $C_5H_8:NMe_2Br$ , has been found, and is obtained on evaporation as a white deliquescent mass which can be converted into a platinochloride of the formula



By further digestion of the solution after it has become neutral, with a fresh quantity of moist silver oxide, a strongly alkaline solution is again obtained; this, when evaporated in a vacuum, yields a viscous brownish syrup which appears to be an ammonium base, as methyl iodide has no action on it. On distillation, it splits up into water and a new base of the formula  $C_5H_7Me:NMe$ . This base is specifically lighter than water, in which it is nearly insoluble, boils at  $137-142^\circ$ , and absorbs carbonic anhydride on exposure to the air. The platinochloride is soluble in water and alcohol. The base unites with methyl iodide with almost explosive violence, yielding a compound of the formula  $C_5H_7Me:NMe_2I$ , readily soluble in water, sparingly soluble in alcohol.

*Dimethylpiperidine dibromide hydrobromide* crystallises in lustrous plates; the numbers obtained on analysis were very unsatisfactory. By the action of potash on an aqueous solution of the substance, an oily base is separated, showing that the substance cannot be an ammonium bromide.

A. J. G.

**$\alpha$ -Isopropylpiperidine.** By A. LADENBURG (*Ber.*, 17, 1676—1679).—Ladenburg and Schrader recently described two isopropylpyridines, one of which was shown to belong to the  $\gamma$ -series (this vol., p. 1048), whilst the constitution of the second one was not established. The higher fraction containing it yields picolinic acid on oxidation, showing that it contains  $\alpha$ -isopropylpyridine. In order to separate the two bases more perfectly than can be effected by fractioning, the author converts them into the corresponding piperidine-bases, and separates these by means of their platinochlorides. A concentrated aqueous solution of the isopropylpiperidine hydrochloride is mixed with the calculated quantity of platinic chloride, the mixture warmed to dissolve the precipitate, and evaporated to a syrup. When cold, a mixture of ether (2 parts) and alcohol (1 part) is added to precipitate the salt of the  $\beta$ -base, whilst that of the  $\alpha$ -base remains in solution.  $\alpha$ -Isopropylpiperidine,  $C_8H_{17}N$ , separated from the purified platinochloride, boils at  $162-164^\circ$ , is sparingly soluble in cold, and still less in hot water. It closely resembles conine in its odour, physiological and other properties, as seen from the following table, the conine employed in the experiments being specially purified by the author.

	Conine.	$\alpha$ -Isopropylpiperidine.
Sp. gr. at $0^\circ$ .....	0.8625	0.8660
Hydrochloride .....	m. p. $218^\circ$	m. p. $206^\circ$
	Both crystallise in needles, are stable in the air, and dissolve readily in water and alcohol.	
Hydrobromide .....	m. p. $207^\circ$	m. p. $216^\circ$
	Both crystallise in prisms, are stable in the air, and are readily soluble.	
Platinochloride .....	Very soluble in water, crystallise with difficulty, soluble also in mixture of alcohol and ether.	
Action of mercuric chloride on the solution of the hydrochloride	None.	None.
Action of gold chloride.....	Oily precipitate in both cases.	
Action of picric acid.....	Both yield an oily precipitate in concentrated solution, no precipitate in dilute solution.	

The small differences are probably connected with the optical inactivity of the artificial base, and will possibly vanish if it be split up into its active constituents, and the dextrorotatory component isolated.

A. K. M.

**The Liquid Alkaloid from *Lupinus Luteus*.** By G. BAUMERT (*Annalen*, **224**, 321—330).—The author discusses the results of Siewert's investigations (*Landw. Versuchs-Stat.*, **27**, 52), Beyer's (*ibid.*, **14**, 161), Schulz's (*Landwirtschaft Jahrbuch*, 1879, 37), and Liebscher's (*Bericht landwirtschaftlichen Inst. Univ. Halle*, **2**, 70) on the alkaloids contained in the yellow lupine, and maintains that his own experiments (*Ber.*, **14**, 1150, 1321, 1880; **15**, 631, 1951, 2745; *Annalen*, **214**, 361; *Landw. Versuchs-Stat.*, **27**, 15, and 30) prove that the liquid portion of the alkaloids yields a platinumchloride of the constant composition  $C_{16}H_{30}N_2 \cdot H_2PtCl_6 + 2H_2O$ . The liquid alkaloid, which is termed *lupinindine*,  $C_8H_{15}N$ , appears to form a crystalline hydrate,  $C_8H_{15}N \cdot H_2O$ . The liquid portion probably consists of a mixture of lupinidine and its hydrate. It does not contain a mixture of different bases as stated by Siewert and Schulz (*loc. cit.*)

The low boiling fraction of the crystalline alkaloids from the lupine contains *lupinine*,  $C_{21}H_{40}N_2O_2$ . W. C. W.

**Action of Acetic Chloride and Anhydride on Lupinine.** By G. BAUMERT (*Annalen*, **224**, 313—321).—A mixture of lupinine hydrochloride and diacetyl-lupinine hydrochloride is formed by the action of acetic chloride on lupinine. A better yield of the acetyl-derivative is obtained by substituting acetic anhydride for the chloride. The product of the reaction is mixed with ether, and the excess of acetic anhydride decomposed by water. After neutralising the free acid with sodium carbonate, soda is added, and the mixture is then well shaken in order that the acetic derivative may dissolve in the ether. On evaporating the ethereal extract, diacetyl-lupinine remains as a heavy oil insoluble in water. It dissolves readily in hydrochloric acid, and with platinum chloride yields a platinumchloride,  $C_{21}H_{38}Ac_2N_2O_2 \cdot H_2PtCl_6$ , crystallising in rhombic plates.

W. C. W.

**Colchicine.** By S. ZEISEL (*Compt. rend.*, **98**, 1587—1588).—The crystals obtained by Houdé from a chloroform solution of colchicine were described by the author in 1883 (*Monatsh. Chem.*). They are not, however, pure colchicine as Houdé supposes, but are a compound of colchicine and chloroform, and the latter can only be removed by dissolving in water and boiling for some time. Dilute mineral acids decompose colchicine into *colchiceïne* and methyl alcohol. Colchiceïne, when heated with concentrated mineral acids at 110—120°, yields a new base, *apocolchiceïne*, methyl alcohol, and acetic acid. When oxidised, colchicine yields a crystalline product, and when reduced in acid or alkaline solution, it yields amorphous products which are difficult to purify.

C. H. B.

**Investigations on Sinapine. I. Sinapic Acid.** By I. REMSEN and R. D. COALE (*Amer. Chem. J.*, **6**, 50—60).—Sinapine thiocyanate was first prepared by Henry and Garot from white mustard seed, and has since been investigated by Babo and Hirschbrunn. 100 lbs. of seed are pressed to remove oils, then extracted with alcohol, and after concentration mixed with a small quantity of an alcoholic solution of potassium thiocyanate, whereupon crystals of the sina-

pine thiocyanate slowly separate. This method is superior to that given by von Babo and Hirschbrum, the product weighing 80 grams. The substance, after recrystallisation, is almost white, and melts at  $176^{\circ}$ . By boiling with baryta-water, it is resolved into sincaline and sinapic acid, which is precipitated as the barium salt. The sinapic acid may be isolated by the action of hydrochloric acid and recrystallisation from alcohol and water. It melts at  $185.6\text{--}192^{\circ}$ . Analyses agree with the original formula  $C_{11}H_{12}O_5$ ; the substance is partly decomposed by boiling with water. Crystalline salts cannot be prepared, but by digesting the acid with calcium and barium carbonates, the existence of the salts  $(C_{11}H_{11}O_5)_2Ca$  and  $(C_{11}H_{11}O_5)_2Ba$  was demonstrated; the above-mentioned insoluble barium salt is  $C_{11}H_{10}O_5Ba$ . Acetic chloride has no action on sinapic acid, but acetic anhydride converts it into the body  $C_{10}H_{10}O_2(OAc).COOH$ , melting at  $281^{\circ}$ ; hence sinapic acid is monobasic, but contains one phenolic hydroxyl, and the possibility of it being derived from the phthalic acids is excluded. Fused with potash, sinapic acid yields a dark-coloured product, apparently containing pyrogallol, and hence it is probably butylenegalic acid,  $COOH.C_6H_2(OH)<\overset{O}{\text{C}}>C_4H_8$ . The synthesis of sinapic acid is being attempted.

H. B.

**Albuminoids.** By DANILEWSKY (*Bull. Soc. Chim.*, **41**, 254—255).—The basicity of myosin depends on the number of amidogen-groups which it contains, and their number varies in myosins of different origin. It always contains a small quantity of magnesium and phosphoric acid, which appear to be combined with organic radicals; although these inorganic constituents may be removed by treatment with dilute acids, the myosin is thereby converted into syntonin. The latter does not exist in living tissues. Syntonin can be converted into myosin, and if the syntonin is optically active the resulting myosin is likewise, and *vice versa*. Optically active myosin and syntonin are rendered optically inactive by boiling for some time with a 10 per cent. solution of hydrochloric acid. Besides myosin, muscular tissue contains a feeble base, analogous to nucleïn, which the author has designated *myostroïne*. At a high temperature, and in presence of dilute acids, this compound yielded syntonin (derived from myosin, which it contained), *chondropeptone*, and *lecithin*, the last of which can also be obtained from the nucleïn of cow's-milk and yeast. Myosin and myostroïne constitute 70 per cent. of the solid residue of muscle. This total quantity is uniformly found in muscle from different sources, but the proportion of the two constituents is subject to considerable variation. It appears that the more active the work done by the muscle, the greater is the proportion of myostroïne which it contains, this compound having been formed at the expense of the myosin.

W. R. D.

**Hemialbumose or Propeptone.** By R. HERTH (*Monatsh. Chem.*, **5**, 266—327).—The incomplete digestion of albumin by pepsine yields solutions containing an albumin, which Schmidt and Muhlheim (*Arch. Anatom. Physiol.*, 1879, 40) style *propeptone*, and



which Salkowski (*Virchow's Arch.*, **81**, 1880) has shown to be identical with Kuhne's *hemialbumose* (this vol., p. 854). This paper contains an account of the author's investigation of this substance, from the results of which the following conclusions, as to the nature of hemialbumose, are drawn. Hemialbumose is a definite body, in composition it is identical with fibrin; it is as insoluble in water as coagulated albumin. Pure hemialbumose is almost insoluble in solutions of common salt, its solubility increasing from a certain limit with the amount of salt in solution. Hemialbumose exhibits a great tendency to combine with acids and alkalis. The compounds with acids are insoluble in salt solutions, consequently it is precipitated as an acid compound by the addition of solutions of sodium chloride and acids. The characters of the solutions of hemialbumose and of the precipitates obtained from its solutions depend on its reaction with alkalis, acids, and salts. Its solutions are coagulated by heat; in this respect it exhibits a gradual change, which is to be attributed to the influences of the solvents. Hemialbumose cannot be regarded as the product of the decomposition of albumin. P. P. B.

**New Forms of Albumose.** By W. KÜHNE and R. CHITTENDEN (*Amer. Chem. J.*, **6**, 31—51).—The authors have already suggested (*Zeits. f. Biol.*, **19**, 159) that hemialbumose is not a simple body, and the terms "soluble" and "insoluble" were applied to it. Noticing an inconstancy in the manner of precipitation by sodium chloride, a new method of preparation was devised, whereby four different forms of albumose are separated. *Protalbumose*, precipitated by excess of sodium chloride, soluble in cold and hot water. *Deuteroalbumose*, precipitated by excess of sodium chloride, insoluble in cold and in boiling water, but on the other hand soluble both in dilute and strong solutions of sodium chloride. *Heteroalbumose*, similar to deuteroalbumose, but insoluble in solutions of sodium chloride. *Dysalbumose*, not precipitated by excess of sodium chloride, but precipitated by sodium chloride and acids; soluble in pure water. Detailed methods are given for preparing these bodies by pepsin digestion from raw fibrin and from Witte's so-called peptone. The mean composition of five samples of protalbumose and their rotatory power are given in the table:—

C.....	50.89	50.39	50.54	51.50	50.55
H.....	6.83	6.74	6.69	6.80	6.85
N.....	17.12	17.12	17.34	17.13	17.01
S.....	1.17	1.07	1.17	0.94	1.07
O.....	23.99	24.68	24.26	23.63	24.52
$[\alpha]_D$ .....	-72.64°	-79.05°	-77.90°	-73.18°	-71.40°

The variation of the angle of rotation is due, at least in part, to the reagents used to render the solutions transparent. The behaviour with a number of reagents is given. Deuteroalbumose has the composition—

C.....	50·47	50·84
H.....	6·81	6·85
N.....	17·20	17·14
S.....	0·87	1·07
O.....	24·65	24·10
$[\alpha]_D$ ....	-74·41°	-79·11

And both protalbumose and deuteroalbumose are to be considered as first hydrates of albumin. H. B.

**Solubility of Vegetable Protein-compounds in Water containing Hydrochloric Acid.** By H. RITTHAUSEN (*J. pr. Chem.* [2], 29, 360—365).—The solvent action of water containing  $\frac{1}{1000}$  to  $\frac{2}{1000}$  part hydrochloric acid on wheat-gluten was first noticed by Bouchardat (*Compt. rend.*, 14, 962). The author finds that large quantities of the albuminoids of some Leguminosæ may be dissolved by this means, and that the greater part is reprecipitated on neutralising with an alkali. The dry precipitate gave all the reactions of undecomposed albuminoids, being wholly and readily soluble in caustic potash, hydrochloric acid, and more or less in water containing 5 per cent. of sodium chloride. The following proportions of albuminoids were extracted from the various leguminous seeds examined :—

Peas yielded .....	9 per cent. albuminoids.	
<i>Vicia faba</i> .....	12	” ”
Yellow lupins.....	32	” ”
White beans .....	10	” ”
<i>Vicia sativa</i> .....	10	” ” P. F. F.

**Studies on Peptonisation.** By T. CHANDELON (*Ber.*, 17, 2143—2151).—In these experiments, barium peroxide was suspended in an aqueous solution of albumin, and a slow stream of carbonic anhydride passed into the liquid, so that the albumin should be subjected to the continual action of freshly-formed (nascent?) hydrogen peroxide. After 48 hours, the liquid no longer coagulated on heating, and was found to contain—(1) a protein-substance closely resembling casein in most properties, but distinguished from it by its rotary power ( $-69\cdot52$ ), and by the non-occurrence of coagulation on heating in sealed tubes at  $135^\circ$ ; (2) a substance closely resembling propeptone; (3) a substance having all the reactions of peptone. As, in the electrolysis of water, hydrogen peroxide is known to be continually formed, an aqueous solution of albumin, acidulated with very dilute acetic acid, was submitted to electrolysis. The products in this case were syntonin, propeptone, and peptone. The author draws attention to the similarity of these products to those obtained with peptic ferments (syntonin, propeptone, and peptone in the case of pepsin and globulin, propeptone and peptone in the case of trypsin), and to the confirmation it affords of the theory that peptonisation is a phenomenon of hydration. A. J. G.

**Corneïn.** By C. F. W. KRUKENBERG (*Ber.*, 17, 1843—1846).—The substance to which this name was given by Valenciennes is prepared

from the skeleton of the asteroïd polypes and other of the lower animal organisms. The skeleton is first treated with cold hydrochloric acid, to remove the inorganic part, and then digested for several days at 38° successively with active peptic and tryptic digestive fluids. *Corneïn* is left as a horn-like residue, and this, when digested with dilute sulphuric acid for several days, yields a hygroscopic substance, which may be obtained crystallised in prisms. *Cornikrystallin* thus prepared is insoluble in concentrated sulphuric acid, in which it may be preserved for years without change. The author has prepared and analysed corneïn from *Rhipidogorgia flabellum*, *Gorgonia verrucosa*, and *Antipathes* (spec.?), and obtained concordant results agreeing with the formula  $C_{31}N_9H_{44}O_{13}$ .

L. T. T.

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## Physiological Chemistry.

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**Elimination of Nitrogen in the Free State from the Animal Body.** By M. GRUBER (*Zeits. f. Biol.*, **19**, 563—568).—From the results of his former experiments, the author concluded that the intake and output of nitrogen balanced one another. Objections have, however, been raised, as his experimental dog lost during the course of the experiment 920 grams body-weight. He has, however, repeated the experiment, maintaining the dog at an almost constant body-weight, with the same results, viz., the intake and output of nitrogen balance each other. Röhmnn found that only a part of nitrates and nitrites, when given to animals, appeared in the urine, and concluded from this that they were converted into ammonia, and in turn decomposed into nitrogen and water. This, however, does not, as the author points out, affect the question, as no nitrates or nitrites are formed in the body, and only a very small quantity of these would be contained in the food taken. J. P. L.

**Determination of the Rate of Consumption of Oxygen in the Tissues by means of the Spectroscope.** By A. DENNIG (*Zeits. f. Biol.*, **19**, 483—500).—The forefinger, usually of the left hand, was bound round with a caoutchouc band; then the period that elapsed from the moment of binding until the disappearance of the two absorption-bands of the oxhæmoglobin was noted.

In the same individual the time varies, according to the hour of the day at which the observation is made. At night it is between 135—146 seconds, in the morning 114—152, and in the afternoon only 92. Children always give much lower figures. Muscular activity, not only walking, but exercising the arms, voluntarily stopping respiration, warming the hand, all produce a diminution of the period, cooling on the other hand increases it even to 300 seconds.

In a series of observations made by the author on patients suffer-

ing from various ailments, a diminution of the period occurs throughout.  
J. P. L.

**Biological Function of Phosphoric Acid.** By A. MAIRET (*Compt. rend.*, 99, 243—246).—The elimination of phosphoric acid is connected with general nutrition, the elimination of phosphates, both of the alkalis and alkaline earths being greater the greater the decomposition of albuminoids, or in other words, the greater the elimination of nitrogen. The effect of muscular exertion on the elimination of phosphoric acid depends on the state of nutrition. Phosphoric acid is used up, and if the exertion is proportionally greater than the amount and quality of the food assimilated, the elimination of nitrogen and alkaline phosphates in the urine is increased; but if the diet is rich and abundant, muscular exertion has no effect on the amount of phosphates eliminated in the urine.

C. H. B.

**Assimilation of Maltose.** By A. DASTRE and E. BOURQUELOT (*Compt. rend.*, 98, 1604—1607).—Solutions of maltose were injected into the blood of the dog, both alone and mixed with glucose or saccharose, and the proportion of the sugars in the urine was estimated. No maltose was excreted in the saliva. The results of the experiments show that maltose is directly assimilated with very nearly the same facility as glucose.

C. H. B.

**Effect of Coffee on the Composition of the Blood and on Nutrition.** By COUTY, GUIMARAES, and NIOBEY (*Compt. rend.*, 99, 85—87).—The authors have extended Guimaraes' researches on the physiological action of coffee, using the methods adopted by Couty and D'Arsonval in their investigations on maté (*Compt. rend.*, 94). They find that coffee diminishes considerably the proportion of gases in the blood, but does not affect the proportion of carbohydrates consumed. In other words, it diminishes the activity of the simple combustions which produce carbonic anhydride. On the other hand, coffee increases very considerably the amount of urea in the blood, and stimulates those complex animal processes which use up nitrogenous substances. It increases the formation and excretion of urea, and also the assimilation of nitrogenous foods such as beef. The tension of the blood, the biliary and salivary secretions, and the temperature, are slightly increased, and the movements of the heart and respiratory organs become somewhat more frequent.

It follows that coffee is a complex aliment, which acts mainly by indirectly modifying the phenomena of nutrition and the general functions. It renders the organism capable of consuming and destroying larger quantities of nitrogenous substances, and may consequently be regarded as an indirect source of available energy.

C. H. B.

**Pathological Formation of Fat.** By LEBEDEFF (*Bied. Centr.*, 1884, 356).—The modern theories propose as the source of the abnormal formation of fat in the liver in cases of phosphoric poisoning—(1) the fat of the food; (2) the carbohydrates; (3) the albuminoids. The first case is most unlikely, as the deposition occurs when a mini-

mun of food is given; (2) the same argument holds good; (3) against this proposal the author, with the aid of experiments, urges that the fat which is deposited three days after the taking of phosphorus amounts to eighty times the quantity which could be produced by the albumin present. The action of phosphorus on the blood causes want of oxygen, suppression of blood-corpuscles, consequently formation of compounds the result of incomplete combustion, physical alteration of the blood, and deposition of incompletely oxidised fat in the liver. The explanation of the migration of fat from the subcutaneous connective tissue into the liver is as follows:—The fat in the connective tissue is not so firmly deposited as that in the parenchymatous tissue, and this is demonstrated by the fact that it is almost impossible to remove the fat from the latter by ether, whereas from the former it is readily removed. Such being the condition of affairs, this fat can be readily removed, passes into the blood, and because of the presence of phosphorus it is not oxidised, and is consequently deposited in the liver. If there is no fat capable of being transmitted in this manner, atrophy of the liver ensues.

E. W. P.

**Action of Heat on the Animal System.** By H. SENATOR (*Bied. Centr.*, 1884, 502).—Heat raises the pressure of the blood, but part of this rise may be due to the movement of the animal under experiment, part to nervous irritation. Breathing is at first more rapid and deeper, later on more rapid only. At high temperatures albumin appears in the urine.

E. W. P.

**Influence of Stature on the Interchange of Matter and Energy.** By M. RUBNER (*Zeits. f. Biol.*, 19, 535—562).—Among many factors which influence the degree of decomposition of matter, the effect of stature has hitherto been least studied. Regnault and Reiset have shown that small animals consume more oxygen relatively than large ones. In the present paper, the author has endeavoured to solve the question for a particular kind of animal, the dog. Different sized dogs were kept under the same conditions of exercise and temperature. The consumption of albumin was determined from the nitrogen found in the urine; and the consumption of fat from the carbon of the carbonic acid expired, and the carbon contained in the urine after subtracting that belonging to the proteid decomposed. The total interchange of matter is calculated in proportion to the calorific values of the compounds consumed. 1 gram of nitrogen corresponds with 25.64 calories, 1 gram of fat with 9.686. The following averages, (p. 1394) reckoned from the amount of urea excreted, were obtained from the experimental results after reducing them to a uniform temperature of 15°.

With the decrease of body-weight, there is a gradual increase of the intensity of combustion. The reason of the high figures obtained in the case of small animals is solely, as the author shows, due to their relatively large surface; the decomposition increases as the surface increases, that is to say, for every square centimetre of surface an equal number of heat-units are given off, consequently the total interchange of matter in starving animals is proportional to their surface.

Body-weight of dog.	Calories per day per kilogram.	Relative formation of heat.
31.2	35.68	100
24.0	40.91	114
19.8	45.87	128
18.2	46.2	129
9.6	65.16	182
6.5	66.07	184
3.2	88.07	247

Large and small dogs consume different quantities of food stuff, because the impulses given off by the skin caused by the cooling of the surface increase the activity of the cells. For equal surfaces approximately isodynamous quantities of matter are consumed. The author concludes that variations produced by loss of heat in every warm-blooded animal are the sole cause of the differences observed between the material consumed and energy expended. From comparisons made by Voit and Kuhein on the consumption of material in starving animals, it is shown that small animals consume more albumin in proportion to fat than large ones, because they possess less fat.

J. P. L.

**The Excretion of Urea and Inorganic Salts with the Urine under the Influence of an Artificially Increased Temperature.**

By C. F. A. KOCH (*Zeits. f. Biol.*, **19**, 447—468).—Several experiments have been made before to determine whether high temperatures caused by artificial means influence the excretion of urea in the same manner as fever; the results, however, were very contradictory. Neumayer and Schleich found that an important increase took place when either men or animals were subjected to warm baths; Bartels, Kaup, and Senator, on the other hand, came to the opposite conclusion, Kaup even observing a slight diminution.

The author has repeated Schleich's experiments, at the same time extending his observations to the excretion of the inorganic salts (phosphates, chlorides, and sulphates). In fever, the chlorides almost wholly disappear. The results are mostly of a negative character. The urea was not increased in any experiment; the phosphates and chlorides show a slight decrease of only very short duration, whilst the sulphates are unaffected. As an increase in the carbonic acid expired takes place in high temperatures, experiments were made to determine whether any direct relation existed between the amount of carbonic acid expired and urea excreted. No such relation could be found.

J. P. L.

**Formation of Urea from Sarcosin.** By E. SALKOWSKI (*Zeits. Physiol. Chem.*, **8**, 149—157).—A controversy between the author and Schiften upon the formation of urea from sarcosin.

J. P. L.

**Influence of Intellectual Activity on the Elimination of Phosphoric Acid by the Urine.** By A. MAIRET (*Compt. rend.*, **99**, 282—285).—The effect of intellectual exertion, like that of muscular exertion, is closely connected with the sufficiency or insufficiency of the diet of the individual. The general result is a diminution in the

quantity of nitrogen and alkaline phosphates eliminated by the urine, the amount of diminution depending on the duration of the intellectual effort. When the diet is insufficient relatively to the work done, an additional effect is produced, and the amount of phosphates of the alkaline earths eliminated is increased. For one and the same diet, the more severe the intellectual effort, the greater is the increase in the elimination of earthy phosphates. With a purely vegetable diet, this increase is particularly well marked. It follows from these results that phosphoric acid is intimately connected with the nutrition and activity of the brain, and that when the brain works it absorbs alkaline phosphates and gives up phosphates of the alkaline earths. Intellectual activity retards general nutrition.

A comparison of these results with those relating to the effect of muscular exertion (this vol., p. 1392) shows that intellectual and muscular activity produce exactly opposite effects; the former diminishes the elimination of nitrogen and alkaline phosphates and increases the elimination of earthy phosphates, whilst the latter diminishes the elimination of earthy phosphates, but increases the elimination of alkaline phosphates and of nitrogen. The effect of general nutrition is exerted alike on both classes of phosphates and on nitrogen.

C. H. B.

**Formation of Mercapturic Acid in the Organism, and its Detection in the Urine.** By E. BAUMANN (*Zeit. Physiol. Chem.*, 8, 190—197).—The urine of animals after feeding with chloro- or bromobenzene does not originally contain the substituted chloro- or bromophenylmercapturic acid, but a body strongly laevorotatory, which on treatment with acids yields mercapturic acid. The author has obtained the potassium salt of this compound, but cannot isolate the free acid, as it is at once decomposed into mercapturic acid and an acid soluble in water and alcohol, which reduces Fehling's solution, and is probably a glyceronic acid. The following is the general method for detecting the mercapturic acid:—The urine is precipitated with lead acetate, the excess afterwards removed with sulphuretted hydrogen, the filtrate boiled for ten minutes with strong soda and a few drops of Fehling's solution, then acidified with hydrochloric acid. If mercapturic acid be present, a yellow caseous precipitate of the copper compound of the mercaptan will be formed. By this reaction it was found that only the halogen-derivatives of benzene and naphthalene formed any considerable quantity of mercapturic acid. Benzotrile gives no trace, but forms, as Giacosa conjectured, the phenolic ethereal sulphate which splits up yielding the nitrile of salicylic or parahydroxybenzoic acid.

J. P. L.

**Inflammable Gases in the Animal Organism.** By B. TACKE (*Ber.*, 17, 1827—1830).—In order to determine whether the inflammable gases generated in the digestive organs of animals pass out of the body by the anus or through the blood by the lungs, the author has made a series of experiments on rabbits. The bodies of the rabbits were surrounded with water, in order to prevent as far as possible the diffusion of these gases through the skin. As the result of these experiments the author finds that, in the case of rabbits, by far the



greater part of the inflammable gases emitted from the body passes out through the lungs, but that a small quantity also passes out by the anus. The author believes that if any oxidation of these inflammable gases takes place during their passage through the blood and lungs, the amount of gas so oxidised is exceedingly small. L. T. T.

**Analyses of Human Milk.** By H. STRUVE (*Bied. Centr.*, 1884, 503).—Healthy human milk contains 3–5 per cent. butter-fat, and is of a sp. gr. 1·031–1·035. When treating the milk with ether, a gelatinous mass is removed, but the quantity is very fluctuating.

E. W. P.

**Influence of Pilocarpine and Atropine on Lactation.** By F. HAMMERBACHER (*Bied. Centr.*, 1884, 503).—The action of these two drugs is to lower for the time the yield of milk, but their action is very transient.

E. W. P.

**Employment of Milch Cows for Labour.** By V. BABO (*Bied. Centr.*, 1884, 502).—It is not advisable to work milch cows when oxen are obtainable, as the former loose more flesh than the oxen, and the yield of milk decreases.

E. W. P.

**Annual Report of Experimental Dairy Farm at Kiel.** By M. SCHRODT (*Bied. Centr.*, 1884, 417).—The report gives the extremes of sp. gr., fat, and dry substance during the year; the average of the whole year for day's milk was 12·30 per cent. dry substance, 3·52 per cent. fat. The variations between morning and evening milk are not unimportant, the dry substance and fat differing from 0·5 to 1 per cent., and sometimes more.

		Sp. gr.	Dry substance.	Fat.
Morning milk	stall fed.....	1·0295–1·0331	11·52–12·63	3·01–3·79
	grass fed ....	1·0307–1·0335	11·24–13·22	2·57–3·05
	stall fed.....	1·0318–1·0338	11·80–12·57	3·17–3·81
Evening milk	stall fed.....	1·0302–1·0330	11·53–12·83	3·14–4·05
	grass fed ....	1·0289–1·0339	11·28–13·92	2·96–4·77
	stall fed.....	1·0321–1·0339	12·20–13·11	3·37–4·15
Day's milk, stall fed.....		1·0300–1·0331	11·32–12·87	2·74–4·14

J. F.

**Composition of Cow's Milk in Holland.** By D. GABEL (*Bied. Centr.*, 1884, 420).—The milk of Dutch cows is known to be poor in fat. 18–20 litres are generally required to make half a kilogram of butter. The following table shows the composition of the milk of a large and carefully conducted dairy at the Hague :—

Month.	No. of expts.	Sp. gr.	Degrees of creamometer.	Solids.	Fat.
May .....	10	1·0313	9·06	12·16	2·82
June .....	5	1·0312	7·00	12·10	2·71
July .....	6	1·0308	8·10	11·88	2·57
August .....	6	1·0306	8·60	11·95	2·55
September .....	4	1·0316	9·50	12·25	2·90
October .....	3	1·0306	12·00	12·20	2·75
November .....	5	1·0310	11·00	12·04	2·60
December .....	4	1·0313	11·20	12·10	2·70
January .....	3	1·0316	10·50	11·67	2·60
February .....	4	1·0306	11·50	12·20	2·88
March .....	4	1·0316	10·00	12·30	2·83

J. F.

**Composition of the Ash of Cow's Milk.** By M. SCHRODT and H. HANSEN (*Landw. Versuchs-Stat.*, **31**, 55—79).—The milk was taken from 10 cows, which had all calved between October and the beginning of the succeeding January; samples were taken at seven different times, from January till September, and analysed with special attention to the ash-constituents: the first three samples were taken while the cows were in the stable, and the rest of the time they were put out to grass. The following table gives the general result of the analyses:—

	1.	2.	3.	4.	5.	6.	7.
K <sub>2</sub> O.....	25·81	26·94	25·18	26·30	26·17	22·55	24·90
Na <sub>2</sub> O .....	11·78	10·39	10·09	11·97	11·42	10·65	10·26
CaO .....	19·71	21·81	21·09	21·26	20·93	23·57	21·77
MgO .....	2·77	2·75	2·75	3·15	1·78	2·66	1·90
Fe <sub>2</sub> O <sub>3</sub> .....	0·13	0·21	0·05	0·08	0·11	traces	0·10
SO <sub>3</sub> .....	4·07	4·15	3·75	4·38	4·20	3·92	4·30
P <sub>2</sub> O <sub>5</sub> .....	23·11	23·11	24·61	22·41	23·59	26·51	25·41
Cl.....	16·15	13·15	15·94	14·16	14·81	13·48	14·52

From the above figures, it is readily seen that there is no marked change in the ash-constituents of the milk at varying periods of lactation. The small differences that are apparent seem to owe their origin to change of fodder rather than to the length of time that the cows had been milked. The increase of the amount of phosphoric acid and lime in the last four analyses is probably due to an increased secretion of casein in the milk during that time, the cows being then in the pasture. The experiments were continued with some of the cows for a few months more, when a more tangible depression in the quantity of potash was noted. The milk of several cows which had just calved showed also less alkali, but a considerable increase in phosphate of lime.

J. K. C.

**Infection of Eggs by Chicken Cholera.** By BARTHÉLEMY (*Bied. Centr.*, 1884, 419).—A hen with the disease, of which she afterwards died, laid 14 eggs which were set to be hatched, but they did not come to maturity—opened between the eighth and tenth day there was found a quantity of black blood, having the peculiar smell of blood from fowls dead of the disease; this blood contained numerous bacteria. It is clear that the secretions of the mother, containing the spores, passed into the substance of the egg, and the shells allowed sufficient oxygen to pass to enable them to develop. J. F.

**Bacillus of Cattle Plague.** By METZDORF (*Bied. Centr.*, 1884, 419—420).—The author has observed a distinctive bacillus in the blood of animals which died of the disease; it was also observed in the coats of the intestinal canal and the lymphatic glands; the microscopic examinations were made on the bodies immediately after death, so that there could not be any question of putrefactive germs. J. F.

**Action of Potassium Ferricyanide on Blood.** By v. MERING (*Zeits. Physiol. Chem.*, 8, 186—189).—Metahæmoglobin is formed by the action of ferricyanide of potassium, only when the red blood corpuscles have been destroyed, either by the addition of water, ether, chloroform, or alternately freezing and thawing, and have yielded their colouring matter to the surrounding fluid. In concentrated solutions, its action is preservative, the same as chloride of sodium and sulphate. J. P. L.

**Poisonous Action of Urea.** By GRÉHANT and QUINQUAUD (*Compt. rend.*, 99, 383—385).—When urea is injected in sufficient quantity under the skin of the frog, guinea-pig, rabbit, pigeon, and dog, it gives rise to tetanic convulsions, similar to those produced by strychnine, followed more or less rapidly by death. The amount of urea in 100 grams of the blood after death was 0·82 gram in the case of the guinea-pig; 0·661 gram in the case of the rabbit, and 0·6 gram in the case of the dog. The amount present in 100 grams of human blood in fatal cases of retention of urine, &c., varied from 0·21 gram to 0·41 gram.

When urea is injected under the skin, the whole of it is never completely absorbed before the animal dies, even if death does not take place until several hours after injection. Urea does not act directly on the muscular fibre, and does not diminish the energy of its contraction. C. H. B.

**Do Bones contain Keratin?** By H. E. SMITH (*Zeits. f. Biol.*, 19, 469—482).—Broesike maintains that the membranes of the Haversian canals of the lacunæ and the canaliculi consist of keratin. The author, to test this assertion, determined anew some of the chief properties of keratin by experimenting on bodies containing it in a pure state. He found that it resisted both the action of pepsine and trypsin; a solution of caustic potash or soda of 20 per cent. dissolved it; 40 per cent. solutions had a weaker action, and a solution of  $\frac{1}{2}$  to 1 per cent. scarcely any action at all. Bones, however, when digested

with pepsine and trypsine, left but an unimportant residue, which, moreover, was completely soluble in a  $\frac{1}{2}$  or 1 per cent. solution of caustic potash or soda, after removal of the fat by ether.

J. P. L.

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## Chemistry of Vegetable Physiology and Agriculture.

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### Action of Oxygen on the Activity of the Lower Organisms.

By F. HOPPE-SEYLER (*Zeits. Physiol. Chem.*, 8, 214—228).—From further researches conducted with the apparatus described in a previous paper, by means of which a continual supply of oxygen can be introduced into the fluid, the author has been led to the conclusion that when oxygen is continuously present, the only certain products formed, during the putrefaction of albuminous liquids, are carbonic anhydride, water, and ammonia, or some closely allied nitrogen compound; neither hydrogen or marsh-gas, indole, nor skatole are formed except perhaps in very small quantities; leucine and tyrosine, too, if formed at all, are only passing stages and do not exist permanently. Thus putrefactive bacteria behave as all other organisms, they assimilate oxygen and eliminate carbonic anhydride, water, and ammonia. In the absence of oxygen, all organisms show more or less evidence of fermentation, but whilst the ordinary putrefactive bacterium can live some time when oxygen is excluded or present in insufficient quantity, all other organisms die off. The bacterium of the cellulose fermentation resists the want of oxygen for a long time. Whether there are organisms that live in the absence of oxygen is not shown. Bacteria multiply quicker in the presence of an excess of oxygen than with an insufficiency.

J. P. L.

**Influence of High Pressures on Putrefaction.** By A. CERTES (*Compt. rend.*, 99, 385—388).—Vegetable and animal infusions in fresh water and sea water putrefy under pressures of from 350 to 500 atmos., but the chemical changes which take place, and the organisms which are developed, seem to be different from those observed when the same solutions ferment under ordinary pressure. Blood containing the bacilli of anthrax lost none of its virulence by being subjected to a pressure of 600 atmos. for 24 hours.

C. H. B.

**Cultivated Wine Yeast.** By A. ROMMIER (*Compt. rend.*, 98, 1594—1596).—The true wine ferment on the skin of the grape requires a considerable time and a comparatively high temperature for its development, and before it attains its full activity other ferments and moulds develop and produce secondary fermentations which impair the quality of the wine. If, however, the fresh must is mixed with a suitable proportion of cultivated wine yeast (about

15 c.c. per kilo.), fermentation takes place rapidly even at temperatures as low as 15—22°, and is complete in about 7 days. If the must is mixed with sugar, the latter is entirely decomposed, but in this case complete fermentation requires a much longer time. The rapidity with which the principal fermentation takes place under these conditions prevents the development of the secondary ferments, and the quality of the wine is much improved. The low temperature at which fermentation takes place, and the short time required for its completion, render this method especially valuable for the production of white wines.

C. H. B.

**Water Culture of Lupines.** By WEISKE (*Landw. Versuch-Stat.*, 30, 437—444).—The fact of lupines producing a crop rich in nitrogen when grown in soils poor in that element has excited much interest, but the author believes that comparatively few cultural experiments have hitherto been made with them. His experiments consisted in growing two sets of plants, one in a nutritive solution containing nitrogen, the second in water free from it. The first set of experiments were unsuccessful, but the second yielded better results, six strong healthy plants were selected, three placed in cylinders containing the one, and three in cylinders filled with the other medium; this was done on 21st June, in the middle of July the plants in the non-nitrogenous fluid ceased growing, and gradually faded. The others on the contrary had finely formed roots, and continued to grow. Other four plants were then taken, two of them placed in cylinders with closely fitting lids bored to let the stem of the plant through, then carefully stopped with wadding so that the roots could not obtain nitrogen either from the air or water, two others were grown in porcelain dishes in filter-paper saturated with nitrogenous solution; after a short time one plant of each set died—as did the others later on: the author gives tabular results of analyses, but owing to comparative failure of the experiments they are not of much value.

J. F.

**Change in the Composition of Potatoes by Ripening.** By SAARE (*Bied. Centr.*, 1884, 322—324).—Measurements of the average size of starch cells are given, and they are for large cells 215 microm., the greatest difference being 80 microm. The smaller potatoes have round, whilst the larger have elongated cells; the smallest cells measured on the average 115 microm. The author divides the grains into firsts, seconds, and thirds, according to size, as follows: 21 microm., 21—12·5 microm., and under 12·5; these latter are lost to the manufacturers, being washed away. The percentage of these qualities varies in ripe tubers according to variety. During ripening, the total weight, size, and number of tubers, size of cells, sp. gr., dry matter, and starch steadily increase, whilst sugar and fibre decrease; when employing the table for calculating available starch from the sp. gr. of tubers, 1·5 per cent. must be deducted and placed to the account of loss: the number of large grains increases as the potato ripens.

E. W. P.

**Influence of Krugite on the Percentage of Starch in Potatoes.**

By KETTE (*Bied. Centr.*, 1884, 355).—The reduction of starch in potatoes by the use of kainite as manure is ascribed to the chlorine present, but if krugite, which contains but very little chlorine, is used, the results are the same—the starch falls considerably in percentage.

E. W. P.

**Absorption of Nitrogen by Leguminous Plants.**

By BOUTELLEAU (*Bied. Centr.*, 1884, 420).—An old vineyard when cleared and manured, was cropped for two years with grain in such quantity that it was calculated all the nitrogen had been exhausted by the corn, yet the third year there was an abundant yield from lucerne and csparssette, sown between the drills.

Another field was well manured with stable manure,  $\frac{1}{3}$  was planted with potatoes,  $\frac{1}{3}$  with maize, and  $\frac{1}{3}$  with vetches, the second year the whole field was sown with wheat, the part where potatoes had been yielded 30 hectolitres, after maize 28 hectolitres, after the vetches 35 hectolitres, although the vetches themselves contained more nitrogen than the maize.

J. F.

**Absorption of Nitrogenous Foodstuffs by Plants.**

By W. O. ATWATER (*Ann. Chim. Phys.* [6], 2, 322–331).—This paper contains an account of a series of experiments carried on during the last seven years in various parts of the United States and Canada. Their object was to ascertain (1) the effect produced on different kinds of plants by the application of mineral manure, such as calcium superphosphate and potassium chloride; (2) the fertilising influence of nitrogen in the form of nitrates and ammoniacal compounds; and (3) the degree of absorption of nitrogen by the plants, from the soil or air.

The experiments were performed with maize, potatoes, and oats; the results may be summed up as follows:—

(1.) Maize absorbs large quantities of the phosphoric acid and potassium chloride manures, but relatively small quantities of nitrogenous substances; it possesses to a high degree the property of obtaining its necessary nitrogen from natural sources. In this respect, maize resembles the Leguminosæ rather than the cereal plants.

(2.) Potatoes seem to be affected by the superphosphates, potash salts, and the nitrogenous manures, and are less apt than maize to procure their nitrogen from natural sources.

(3.) Oats are more sensible than potatoes to a defect of nitrogen, and are more profited by the addition of that element in the form of manure.

V. H. V.

**Influence of Water on the Growth of Plants.**

By HELLRIEGEL (*Bied. Centr.*, 1884, 475–484).—The questions to be answered were: How much water does a plant transpire under normal conditions? How much water must be present in the soil? And how is the proper quantity of water to be retained? Barley was sown in quartz sand, to which had been added sufficient plant-food, and the amount of water present was 60 per cent. of the whole retainable water. The observations showed that the evaporation was much more dependent

on the temperature of the air than on the evaporating surfaces; a rising temperature with dryness increased the evaporation, and *vice versa*. When the temperature remains constant, then the moistness of the air greatly affects the evaporation, which may in dry air be raised to double, and in moist air reduced to one-half that which is evaporated under normal conditions; but this alteration has no effect on the physiological functions of the plant so long as the condition of soil remains normal. A long account of the construction of the apparatus used in this research is given. The rapidity of the air currents has much influence on the evaporation, but the effect is much less than those exerted by warmth and moisture. To observe the effect of light, two healthy and well-grown barley plants were examined, the one under a bell-jar painted white, the other under a clear glass jar, both of them connected with the ventilating apparatus above referred to; other coloured shades were also employed, but all with a similar result, that light has a very considerable influence, but not so great as that exercised by heat and moisture.

Experimenting with sunflowers, the author finds that the rise of the sap is independent of the leaves, and that moisture is carried up by the roots, so long as there is a certain degree of water in the soil; the minimum of moisture seems to be slightly above 8 per cent. of the dried soil.

E. W. P.

**Formation of Diastatic Ferments in the Cells of the Higher Plants.** By W. DETMER (*Ann. Agronomiques*, 10, 280—281).—Ungerminated grains of wheat contain a little diastatic ferment, but the presence of oxygen is necessary to the further development of this ferment by germination.

J. M. H. M.

**Relation of Red Colouring Matter of the Phanerogams to the Migration of Starch.** By H. PICK (*Ann. Agronomiques*, 10, 274—276; from *Bot. Centralblatt*, 16, 281, 314, 343, 375).—In many of the phanerogams, different organs or parts of organs are coloured red, either permanently or at certain periods of their life. The author brings together a number of observations on the formation and optical properties of this red colouring matter, and on its relation to the transportation of starch at certain phases of a plant's life. It seems probable that the colouring matter is derived from tannin, since it is especially noticeable in tannin-producing plants, and experiments seem to show that as the red colour of young leaves increases, so the tannin decreases. The colouring matter itself gives some of the reactions of tannin. In stems, leaves, and fruits (*e.g.*, apples), the red colour is only developed on the parts exposed to light, and young plants which remain uncoloured so long as they are kept in the dark, speedily redden on exposure to light, which may be white, blue, or red indifferently. The absorption-spectrum of the red colour is almost exactly complementary to that of chlorophyll. By exposing portions of a growing leaf of the castor-oil plant under ruby glass, or under a solution of the red colouring matter obtained from beetroot, the author shows that at the end of 15 minutes of sunlight the starch contained in the outer layers of cells has almost entirely migrated to the subjacent



cells of the circulatory tissues. By exposure to direct solar light, on the contrary, it is the outer layers of cells which become charged with starch granules. By causing the leaf of a French bean to absorb a solution of sugar, starch may be made to accumulate in the cell layers; on exposing the leaf to red light this starch also migrates to the subjacent tissues.

With regard to the autumnal colouring of leaves, the lower temperature increases the formation of tannin, which becomes changed into the red colouring matter; the starch accumulates by preference in the coloured cells, and disappears with the fall of the leaf.

J. M. H. M.

**Osmotic Functions of Living Parenchyma.** By WESTERMAIER (*Ann. Agronomiques*, 10, 271—273).—An account of the part taken, according to the author's theory, by the ligneous parenchyma and medullary tissue in causing the ascent of the sap. An experiment with parenchyma is adduced in support of it.

J. M. H. M.

**Absorption of Water by Flower Petals.** By A. BURGERSTEIN (*Bied. Centr.*, 1884, 422).—The petals of several kinds of composite plants have the property of absorbing moisture, and the underside of the petals is more active than the upper.

J. F.

**Transpiration in Plants in the Tropics.** By V. MARCANO (*Compt. rend.*, 99, 53—55).—The evaporation of water from the leaves of plants in the tropics is practically the same during the night as during the day. One-half to three-quarters of the total evaporation during the day takes place between 6 A.M. and mid-day, the maximum being reached between 10.15 A.M. and noon, whilst from noon to 6 P.M. there is very little evaporation. Evaporation is not sensibly affected by the hygrometric condition of the atmosphere. The maximum in the morning corresponds exactly with the minimum pressure of the sap.

C. H. B.

**Chemical Phenomena of the Respiration of Plants.** By T. L. PHIPSON (*Chem. News*, 50, 37).—The author showed in a previous paper (*Chem. News*, 1883) a simple apparatus by which unicellular algæ, supplied constantly with fresh spring-water and exposed to sunlight, gave a constant evolution of oxygen gas. When the carbonic anhydride of the spring-water is exhausted, fresh spring-water is let into the apparatus, whilst the old water is run off, and the evolution of oxygen continues. Instead of renewing the water, carbonic anhydride was supplied to the water after three or four days' running had exhausted its faculty of causing the algæ to give off oxygen. The faculty of evolving oxygen was restored, but not to any great extent, and it became less and less manifest with successive additions of carbonic anhydride.

Experiments show that plants exposed to sunlight are incapable of evolving oxygen in spring-water which has been thoroughly boiled for five minutes, then rapidly cooled and supplied, when cold, with small or large quantities of carbonic anhydride. Evidently something else is required by the plant, and this is hydrogen peroxide, which is decom-

posed by boiling the water. Its presence can be demonstrated in all spring-water, and it is as essential to the life of the plant as carbonic anhydride is. "Respiration" of plants is due to the reaction which occurs in the plant-cell, between carbonic anhydride and hydrogen peroxide, oxygen being evolved whilst ternary compounds are formed in the plant-cell.

When spring-water is boiled, the air collected (after absorption of carbonic anhydride) contains 30-33 per cent. of oxygen, instead of 21 per cent. This difference is chiefly due to oxygen in the state of hydrogen peroxide.

Manganese peroxide in spring-water exposed to strong sunlight can be made to "breathe" like the unicellular algæ. Unicellular algæ in spring-water which has been impregnated with carbonic anhydride after boiling (and so deprived of its hydrogen peroxide), and having abundant contact with the air, will, after several days' exposure to the sun, evolve small quantities of oxygen, showing that, in these circumstances, hydrogen peroxide is slowly formed again.

J. T.

**Effect of Depth of Sowing on the Germination and Growth of Plants.** By E. WOLLNY (*Bied. Centr.*, 1884, 293-299).—There are no definite results obtained by the experiments described, but the general outcome seems to be that the deeper the seeds or tubers are laid in the soil the more irregular and the later do the plants appear above ground, and there seems to be a definite depth for each kind of seed; but this is again dependent on weather and soil. In experiments with rye, it appeared that deeply sown seed suffered much more from winter cold than the shallow sown seeds, and when potatoes are set deep there is less chance of their being attacked by disease.

E. W. P.

**Ratio of Nitrogen to Phosphoric Acid in Seeds.** By E. HEIDEN and others (*Bied. Centr.*, 1884, 484-486).—W. Mayer and Arendt have both stated that there exists a definite ratio between the above components of seeds, and Siegert considers, in the case of wheat and rye, that the percentage is affected by manuring; Ritt-hausen and Pott are of similar opinion, whilst Kreusler and Kern believe that phosphates reduce the nitrogen in the seed. The author has experimented with oats, rye, vetches, and peas, and finds that straw crops are rendered richer in protein by the use of nitrogenous manures, but that by the use of phosphates alone the albumin is neither raised nor depressed. He finds also that the ratio of phosphoric acid to nitrogen in oats and rye is wider than is stated by Mayer, viz., 1:1.20-1:2.13 (oats) and 1:1.44-1.267 (rye). With the other crops, nitrogen does not increase the albumin, but phosphates lower it.

E. W. P.

**Composition of American Wheat.** By C. RICHARDSON (*Bied. Centr.*, 1884, 420-421).—The author has examined more than 200 samples of American wheat; it will be seen that it contains less moisture, cellulose, and albumin than European wheat. The principal ingredients fluctuate between the following limits:—

	Minimum.	Maximum.	Difference.
Water.....	6.05	13.52	6.47
Ash.....	6.80	2.98	2.18
Fat.....	1.39	3.93	2.54
Starch.....	67.95	78.95	11.00
Cellulose.....	0.44	2.76	2.32
Nitrogenous matter.... }	8.05	17.10	9.05

The variations in the nitrogenous matter are large, but in other countries there are even greater differences, and the grain in North America has not yet attained its maximum of nitrogen.

The small amount of moisture is attributed to the American method of harvesting. With the exception of Minnesota, Dakota, and Colorado, American wheats are poorer in nitrogen than those of any other country; the grain from the Atlantic States is the poorest, and it is a curious fact that, as a rule, the grain from those States is smaller than in the Western and Pacific States. J. F.

**Analysis of American Barley.** (*Bied. Centr.*, 1884, 491).—Analyses of several American barleys show that they are of a higher class than is generally supposed, and are capable of making quite as good malt as German and Austrian grain. E. W. P.

**Occurrence of Vicin in Broad Beans (*Vicia faba*).** By H. RITTHAUSEN (*J. pr. Chem.* [2], 29, 359—360).—This substance,  $C_{28}H_{51}N_{11}O_{21}$ , was formerly found by the author (*Abstr.*, 1881, 1158) in the seed of *Vicia sativa*, he now finds it in *V. faba* and *V. minor*. The finely-ground beans are extracted with alcohol (85 per cent.), and the residue obtained after distilling off the alcohol is shaken up with ether to remove the fats, when a substance separates in thin colourless needles, which give the characteristic reaction for vicin, viz., after boiling with a few drops of hydrochloric acid, and allowing to cool, a deep blue solution is obtained on adding a trace of ferric chloride and then ammonia in excess. P. F. F.

**Composition of Lupines.** By E. FLECHSIG (*Landw. Versuch.-Stat.*, 30, 445—447).—This paper is a report of numerous analyses of the seeds and stalks of lupines. Full details are given in tables which accompany it—one of them presents a summary of results (p. 1406). It will be observed that there is a great difference between the nitrogenous contents of the different varieties. *L. Cruikshanksii* heads the list with 47.13 per cent. protein, the lowest being *L. hirsutis* with only 27.81 per cent.; their contents in alkaloids, estimated by Tauber, are also very variable. *L. albus*, which is unfitted for cattle food, because of its great bitterness, contains less than other varieties which are readily eaten; bitterness is therefore not a measure of the alkaloids present; the amount of fat also is very variable, and varieties containing most of it have least woody fibre.

*Lupine Seeds.*

Name of variety.	Crude protein.	Nitrogenous extract.	Ethereal extract less alkaloid.	Alkaloids.	Woody fibre.	Ash.
Lup. luteus.....	46·13	29·74	6·53	0·81	13·01	3·78
White seeded yellow.....	46·88	28·48	6·48	0·70	13·34	4·12
L. hirsutus.....	27·81	44·97	8·50	0·02	15·91	2·79
„ albus .....	37·31	36·02	13·01	0·51	10·21	2·94
Large seeded white blue flower	36·19	40·76	7·47	0·27	12·55	2·76
L. termis .....	37·44	37·91	12·53	0·39	9·36	2·37
„ Cruikshanksii .....	47·13	25·66	15·83	1·00	6·74	3·64
„ angustifolius .....	35·94	40·26	7·44	0·25	13·33	2·78
„ blue lupine .....	36·31	40·61	7·72	0·29	12·29	2·78
„ white seeded blue flower	37·94	38·48	8·38	0·37	12·10	2·75
„ linifolius .....	35·56	39·64	7·95	0·32	12·71	2·73
„ polyphyllus .....	43·25	32·01	12·66	0·48	10·97	3·82

*Lupine Straw.*

Name of variety.	Crude protein.	Nitrogenous extract.	Ethereal extract.	Woody fibre.	Ash.
Lup. luteus.....	7·25	34·31	2·26	50·18	6·00
White seeded yellow.....	6·94	32·43	2·88	52·22	5·53
L. hirsutus .....	4·25	38·35	1·66	52·06	3·68
„ albus .....	3·31	35·61	2·04	56·30	2·74
Large seeded white blue flower. .	3·94	35·11	1·31	56·52	3·12
L. termis .....	3·31	34·07	1·27	58·03	3·32
„ Cruikshanksii .....	8·69	33·43	1·56	51·11	5·21
„ angustifolius .....	4·19	30·91	0·87	60·69	3·34
„ blue lupine .....	3·50	32·95	1·60	58·42	3·53
„ white seeded blue flower.....	2·13	35·23	1·57	56·99	4·08
„ linifolius .....	4·19	34·94	1·90	54·93	4·04
„ polyphyllus .....	—	—	—	—	—

J. F.

**Peronospora Viticola.** By E. MACH (*Bied. Centr.*, 1884, 495).—  
The following are analyses of grapes from infected vines :—

	Sugar.	Non-saccharine.	Acids.
Negrara.....	5.93 p.c.	3.81 p.c.	16.9 p.c.
Rossara.....	5.38 „	3.96 „	17.1 „
Gropello .....	10.12 „	3.50 „	12.7 „
Negrara (green) ..	3.37 „	5.38 „	27.3 „
„ better qual- ity .....	3.92 „	3.78 „	18.4 „
Negrara, best ....	5.41 „	3.83 „	18.4 „

E. W. P.

**Poisonous Effects of Arsenic, Zinc, and Lead, on Vegetable Organisms.** By F. NOBBE and others (*Landw. Versuchs-Stat.*, 30, 381—422).—These experiments were undertaken to ascertain the effects of applying those metals directly to plants in process of growth: the subjects of experiment were plants of peas, oats, maize, and buckwheat. The mode of culture was that known as water culture, in large glass cylinders supplied with the nutritive solution employed at the experimental station of Tharaud; the arsenic was added to the different vessels in the form of potassium arsenite, in four degrees of strength, viz., 3, 33, 333, 1000 mgrms. As per litre.

The plants were introduced into the vessels in a healthy condition, and similar plants were reserved as control. In all cases, the results were fatal, but the time varied not a little, the plants treated with the least quantity recovering for a brief period, but eventually succumbing. With all the plants, the upper leaves were first affected, the decay gradually attacking the stems; the appearance of the roots was peculiar, their growth ceased, and they became tinged with a yellow shade. Four plants of maize were taken and tested for arsenic; that treated with 3 mgrms. arsenic yielded none, that with 33 mgrms. nothing, with 333 mgrms. equal to 0.1 mgrm., and that with 1000 mgrms. 0.5 mgrm.  $\text{AsO}_3$ .

The authors think that the action of the arsenic consists either in causing an excessive transpiration from the plants, or that it prevents the absorption of moisture by the roots. This induced them to make further experiments with plants in a dark atmosphere saturated with moisture, which they obtained by growing them under bell-glasses with necessary precautions; as usual, growing similar plants to control the experiments. Both sets died, but those under glasses more slowly than the others, and the result leads the authors to believe the protoplasm of the root cells is the vulnerable point, the poison destroying the power of osmose by the roots.

Further experiments were made as to the limit of dilution which would be injurious to vegetation, and it was found that the presence of As 1 to 1,000,000 = 1 mgrm. of As per litre, exercised a decidedly injurious effect on the normal growth.

The authors next directed their attention to the quantitative estimation of the arsenic actually absorbed by the plants, and give the results in tables, which show the quantities to be extremely minute, the roots containing most and the leaves least.

In order to ascertain the rapidity of absorption, several experiments were made by submitting plants to the influence of the poison for

periods varying from five minutes to an hour, then carefully washing the roots and replacing the plants in the normal solution, it was found that some possessed greater powers of resistance than others.

Experiments with salts of lead and zinc were made in a similar manner; the effects of the latter were very similar to those of arsenic, the death of the plant rapidly following considerable doses: the salts of lead are not so poisonous to vegetation as zinc;  $\frac{1}{1000}$ th part of the latter killed a plant in three days, while another plant treated with the lead salt of same strength lasted 41 days. Carbonate of zinc is the most injurious of all the salts tried, and the plants absorb more of the metal from it. The solutions were daily agitated, so that the roots came well into actual contact with the insoluble precipitates, in fact, were covered with the suspended matter. Both metals are therefore poisonous, and in small quantities act by decreasing the yield of the plant.

The article contains several tables of details and descriptions of the processes employed by the authors for the estimation of the three metals.

J. F.

**Behaviour of Zinc Salts with Plants and in the Soil.** By A. BAUMANN (*Landw. Versuchs-Stat.*, **31**, 1—53).—In view of the conflicting statements made by various writers as to the action of zinc salts on plants, the author set himself to work to thoroughly investigate this subject. The experiments of Freytag had shown that in a soil containing 5 per cent. of zinc oxide various kinds of cereals flourish, and absorb also a small quantity of zinc, but no attention had been given to the nature of the soil used. The author began first by determining the action of zinc sulphate on plants grown in a nourishing solution containing calcium and potassium nitrates, iron and potassium phosphates, and magnesium sulphate. To these was added zinc sulphate in varying proportions, so that four solutions were obtained containing 10, 5, 1, and 0.1 mgrm. Zn per litre respectively.

Thirteen species of plants of seven different families were experimented on, and in each case the plants were chosen as nearly as possible alike, and one of each sort placed in the solution above described, but containing no zinc. The results showed that the action of zinc sulphate when given to the plant in solution is more injurious than has generally been supposed. All plants, with the exception of the Coniferae, speedily die in a solution containing 10 mgrms. zinc to the litre, although traces of zinc in solution are harmless: the proportion in which all the plants thrive undisturbed was 1 mgrm. per litre, the only exception being *Raphanus sativus*. The limit at which the injurious action begins lies between 1 and 5 mgrms. per litre; the only plant that survived a 5 mgrm. solution, with the exception of the Coniferae, was *Onobrychis sativa*. The latter also resisted longest the action of the 10 mgrms. solution, dying in 194 days, while *Trifolium pratense* died in 16 days, and the Coniferae flourished undisturbed. Older plants of the same kind perish sooner than younger ones, probably because of the greater number of leaves in the former and the relatively increased transpiration,

so that greater quantities of the poison are absorbed in a given time. The action of the zinc always shows itself by a change in the green colour of the leaves. When, however, the zinc solution is poured on to the soil, its action on plants growing therein may differ according to the nature of the soil: this was made evident by experiments with the same plants employed before, but grown in two kinds of soil—one a lime soil rich in humus; the other sandy, free from humus, and containing very little lime. The plants were set in pots, there being six experiments with each species, three in lime and three in sandy soil. Two pots (one of each kind of soil) were treated every day with distilled water, two with a solution of 20 mgrms. Zn per litre, and two with a solution of 40 mgrms. In the sandy soil, all the plants treated with zinc solution died, showing that the soil was not able to convert the zinc sulphate into insoluble and harmless forms. With the calcareous soil, however, the case was different; the plants thrived better which had the zinc solution poured on them, doubtless because other elements, such as potassium, calcium, and magnesium were thereby converted into soluble forms. The action of the zinc seemed therefore to depend on the composition of the soil, and further experiments were made to ascertain the quantity of zinc rendered insoluble by passing through various soils. The results showed that the absorptive power of a pure humus soil is the greatest: wood humus absorbed 200 times as much as the sandy soil above referred to, and over 800 times the amount absorbed by a sandy soil from the keuper. Next to pure humus in absorptive power came a rich clayey soil containing lime, then the other soils according to their richness in humus and alkaline earths. Alumina appears to be a very active agent in rendering zinc sulphate insoluble, the sulphuric acid being also thrown down at the same time. The presence of zeolites in soils causes a decomposition of zinc sulphate, sulphates of calcium, magnesium, &c., going into solution. Direct experiments with calcium and magnesium carbonates showed that these have the power of precipitating the whole of the zinc from solution.

The question as to whether insoluble zinc salts, introduced as such into the soil, prove injurious to plants has been answered by all previous workers in the negative. The author tried the solubility of zinc carbonate and sulphide in water charged with carbonic acid, and found that solution took place in both cases to a considerable extent, so much so, that plants immersed in the liquid perished as in solutions of zinc sulphate: the action of the carbonic acid was, however, considerably lessened by the presence of other carbonates, so that this fact can have no bearing on the solution of zinc by water in the soil, at least not to any injurious extent: he concludes, therefore, that insoluble zinc salts in the soil are harmless to plants.

The specific action of zinc on the vegetable organism consists in a destruction of the chlorophyll colouring matter, and a consequent stoppage of the whole process of assimilation.

J. K. C.

**Ensilage.** By WEISKE and others (*Bied. Centr.*, 1884, 464—469).—Lupines, maize, and lucerne were siloed in barrels, and after some time the silage was analysed and compared with the fresh substance.

The analyses were conducted in the usual way after the silage had been extracted with cold water and the volatile acids (butyric) estimated in the extract by volatilisation, and the non-volatile (lactic) by titration. Below are given the analytical results.

Lupines (fresh) lost 3 per cent. water and 22 per cent. dry matter.

	Fresh.	Silage.
Nitrogenous matter ....	20.88	19.88
Oils, &c. ....	4.48	13.48 { 2.30 p.c. lactic 3.58 „ butyric
Fibre .....	30.19	31.57
Extractive .....	38.22	28.03
Ash .....	6.23	7.04

Maize (stamped solid) after 112 days lost 2.4 per cent. H<sub>2</sub>O and 26.1 per cent. solids.

	Fresh.	Silage.
Nitrogenous .....	9.50	8.00
Ether extract .....	2.14	13.43 { 3.47 lactic 7.45 butyric
Fibre .....	33.89	32.39
Extractive .....	42.29	34.55
Ash .....	12.18	11.63

Maize loosely packed lost 35.8 per cent. dry matter.

Nitrogenous .....	9.31	6.63
Ether extract .....	2.42	11.06 { 2.31 lactic 7.34 butyric
Fibre .....	32.37	35.60
Non-nitrogenous .....	45.02	34.84
Ash .....	10.88	11.87

Lucerne was siloed closely (1), slightly pressed (2), and not pressed at all (3), with the following results:—

	1.		2.		3.	
	Fresh.	Silage.	Fresh.	Silage (alkaline).	Fresh.	Silage (alkaline).
Loss of water .....	3.8		—		4.2	
„ dry matter ..	27.1		28.50		30.3	
Nitrogenous .....	26.69	23.25	25.94	21.44	25.00	20.94
Ether extract .....	4.44	8.79	4.91	8.58	5.01	6.75
Fibre .....	22.54	28.03	22.90	30.40	23.57	29.62
Non-nitrogenous ....	37.12	28.52	37.32	26.83	37.52	30.20
Ash .....	9.21	11.41	8.93	12.75	8.90	12.49

Holdeffeiss examined two specimens of green maize silage which had



lost, the one about 40—50 per cent. dry matter, the other about 10 per cent., and this latter had laid in cocks on the field for four weeks. He recommends this plan, as a good fodder is produced, and the harvesting does not clash with that of the potatoes and roots. Wood gives analyses of hay silo which contained 0.34—0.55 per cent. acetic acid. G. Nasir has followed Goffart's method, in which the silage does not become acid, and finds it successful. (See Fry's method in "Mark Lane Express," 1884. Abstractor.) E. W. P.

**Presence of Mildew, &c., in Cattle-foods.** By A. EMMERLING (*Bied. Centr.*, 1884, 472—475).—Various forms of fungoid growths have been found in earth-nut and other cakes, and may be obtained by treating the powdered cake with a little water for 24 hours at 35°. The principal forms of schizomycetes observed were micrococcus, bacteria, and bacilli; at times leptothrix and cladothrix were observed, and in a few cases sarcina and spirilla. Of the 52 samples, 61 per cent. contained some of these growths; of cotton-cake and meal, 40 per cent. were infected, many containing a very high percentage of bacteria and bacilli, and it is to the presence of so many in this kind of food that the ills which often follow its use may be ascribed. Short accounts about several other cakes (linseed, &c.) are given. E. W. P.

**Cotton-cake as Fodder for Milch-cows.** By DE LA TRÉHONNAIS (*Bied. Centr.*, 1884, 311).—Under adverse circumstances decorticated cotton-cake considerably raised the yield of milk. E. W. P.

**Cultivation of Potatoes.** By J. TIMM and others (*Bied. Centr.*, 1884, 487—490).—Timm finds Chicago Early the heaviest cropper, and that Richter's Imperator is the best to grow for importation to England. An anonymous writer has tried growing large and small sets to discover which gives the best yield, and finds that it is best to set one large set (say 100 grams) instead of smaller sets of 25 grams; also that 4 sets of 25 grams apiece yield as well as one set of 100 grams. Märcker has come to a similar conclusion. E. W. P.

**Horse-chestnuts as Cattle-food.** By KAEHLER (*Bied. Centr.*, 1884, 386).—According to the author, the fruit of the horse-chestnut deserves more attention as fodder than it has yet received; he has fed cattle with it for eight years, the only objection being the smallness of the supply. He gave each animal 2 metzen (about 7 litres) twice daily; they were eaten readily, especially when young, when they just commenced to fall. Swine did not take to them so readily, but the author thinks that if they were shelled and deprived of their bitter principle they would be eaten. A small stock of Southdown sheep was fed regularly every winter. Some of the chestnuts were dried and ground; they were then readily eaten by young cattle. Klein's analysis gave for the meal 10.06 per cent. of protein, 4.83 per cent. of ash. J. F.

**Drying of Exhausted Beet-residues.** By J. H. REINHART (*Bied. Centr.*, 1884, 415).—The exhausted sections of beet are found to yield

a very large proportion of their moisture to pressure, provided they have been previously torn so as to open the cells. A mass is thus obtained containing 20—40 per cent. dry matter, easily treated afterwards by ordinary means of drying, and capable of being made into convenient cakes, &c., for purposes of fodder. J. F.

**How to bring Heavy Raw Soils into Cultivation.** By E. HEIDEN and others (*Bied. Centr.*, 1884, 437—446).—These experiments were conducted during the years 1869—78, and had for their object the most economical and satisfactory treatment of uncultivated land, so as to render it fit for cropping. The manures were lime, potassium and ammonium sulphate, and calcium phosphate, the crops being cereals, leguminosæ, and potatoes. Full details of the experiments are given, accompanied by several tables. The results are as follows:—First season: lime in autumn, plough in and ridge, and in spring plant potatoes, but not straw crop, giving also nitrogen and phosphates; next follow with oats manured as for potatoes, afterwards vetches or peas with bone-meal, again leaving the ground in the ridge during winter. Fourth crop should be potatoes with potash as kainite, this mixed with soil should be ploughed in with stubble, and nitrogen and phosphates applied in spring. E. W. P.

**Preparation of Farmyard Manure.** By P. P. DEHÉRAIN (*Compt. rend.*, 99, 45—47).—Straw oxidises only under the influence of an aërobic ferment, and seems to be free, as a rule, from active anaërobic ferments. Farmyard manure can undergo two kinds of fermentation, viz., neutral, in which carbonic anhydride, methane, and nitrogen are given off, and acid, in which carbonic anhydride, nitrogen, and hydrogen are evolved, and butyric acid is formed. Occasionally both kinds of fermentation take place at once, and the evolved gases contain both methane and hydrogen, but in such case one gas is always present in much larger proportion than the other. It seems probable that the anaërobic ferments present in farmyard manure are derived from the alimentary canals of the animals, and according to their relative abundance and the conditions in which they are placed, they produce one or the other kind of fermentation. C. H. B.

**Fermentations of Farmyard Manure.** By P. P. DEHÉRAIN (*Ann. Agronomiques*, 10, 385—409).—*Aërobic Fermentation of Straw.*—At 40° straw cut into small pieces and moistened with water gives rise to an evolution of carbonic anhydride which is nearly constant for the first few days and then gradually diminishes. This action is due to microbes, for it is almost entirely prevented by chloroform. The liquid contains a multitude of small and very active vibrios. At 110° and 120°, however, slight oxidation occurs without the intervention of ferments.

*Aërobic Fermentation of Manure.*—The gases evolved by different layers of a manure heap in different stages of fermentation have been examined. The gas evolved near the top of a heap is composed of carbonic anhydride and nitrogen, that from the middle contains

marsh-gas in addition, and that from the bottom, when there is no access of air, often contains nothing but carbonic anhydride and marsh-gas. The rise in temperature of a fermenting dung-heap is occasioned entirely by atmospheric oxidation, and does not take place if air be excluded, but the production of marsh-gas goes on in the absence of air. A drop of liquid from a fermenting dung-heap is found to be full of very active elongated microbes refracting light strongly when not exactly in focus; they are much larger than the organisms found in the infusion of straw. The oxidation of the carbon of this liquid is greatly diminished but not prevented by the addition of chloroform; the evolution of carbonic anhydride in a dung-heap appears therefore to be due partly to fermentation and partly to simple oxidation.

*Anaërobic Fermentation of Straw.*—If cut straw be placed in water and kept at 40—45° with or without the addition of alkaline phosphates, anaërobic fermentation occasionally takes place as soon as the oxygen of the liquid has been used up, and results in the production of hydrogen or marsh-gas. This fermentation is however exceptional.

The marsh-gas fermentation of farmyard manure may be observed by placing the manure in a flask and collecting the evolved gas over mercury. The evolution of gas proceeds for some days and then almost stops; it may be renewed by temporary exposure of the contents of the flask to the air; after a few days it will again stop, and may be renewed as before. If the flask is heated for some hours at 85°, or if chloroform is added, the production of marsh-gas ceases. The liquid portion of the manure contains short brilliant vibrios, accompanied by a great number of spores. An alkaline reaction is maintained throughout the fermentation. Occasionally hydrogen instead of marsh-gas is produced by the fermentation of farmyard manure; in this case an acid is developed, which appears to be butyric acid. The organism present in this case is exactly similar to that which is present when marsh-gas is produced, and does not resemble the ordinary butyric ferment. When a solution of sugar or dextrin with suitable minerals is fermented with a drop or two of the liquor from a manure heap, hydrogen is produced, but when paper is used instead of sugar or dextrin the fermentation is slower, and marsh-gas is evolved. Sometimes, however, the two gases appear together whichever material is employed. When straw is used as the subject of a fermentation excited by a drop of manure liquor, marsh-gas is more frequently produced, generally free from hydrogen, but sometimes mixed with it. As much as 500 c.c. of gas can be obtained from 10 grams of straw in 48 hours. On the whole it appears probable that there are two distinct ferments, one causing the evolution of hydrogen and the other that of marsh-gas, and that they are conveyed to the manure heap from the intestinal canals of farm animals. Tappeiner has found in the intestinal canal of the Herbivora organisms which attack cellulose, and cause the evolution of the two gases mentioned.

J. M. H. M.

**Loss of Nitrogen during the Fermentation of Farmyard Manure.** By H. JOULIE (*Ann. Agronomiques*, 10, 289—301).—Six

mixtures were made of broken straw 75 grams, horse-droppings 50 grams, putrid urine (human) 300 c.c., and distilled water 275 c.c. Each of these mixtures was placed in an inverted bell-glass furnished with a tubulure, through which passed a cork and glass tube to conduct away the excess of liquid into a conical beaker. To restrict evaporation, the bell-glasses were covered with glass plates. The first mixture received no addition. To the other five were added: (2), 10 grams of mineral phosphate of lime; (3), 10 grams mineral phosphate and 10 grams of gypsum; (4), 10 grams mineral phosphate and 10 grams calcium carbonate; (5), 10 grams calcium carbonate; and (6), 10 grams gypsum. A seventh mixture was also made of straw 150 grams, horse-droppings 200 grams, urine 400 c.c., water 850 c.c., and this mixture was placed in a larger bell-glass than the rest, so as to expose a greater surface to the air. The mixtures were allowed to remain from February 18th, 1883, to September 1st, 1883, and every two or three days the liquor in the beakers (representing the drainings from a dung-hill) was poured back over the manure in the bell-glasses. On April 15, there not being enough liquid to moisten the samples, 100 c.c. of water was added to each. On September 1st, 1883, the experiments were terminated by transferring the liquid portion of each mixture to a litre flask, and making up to the mark with the washings from the solid portion. The amount of dry matter contained in solid and liquid was estimated in each case, and compared with that originally present. The humus acids contained in the several liquors were also estimated by precipitation with hydrochloric acid, and the nitrogen present in the three forms (nitric, ammoniacal, and organic) was determined in both the solid and liquid portions of each sample. In addition, complete analyses were made of Nos. 1 and 7 (which received no addition), proving them to have the same general composition as well fermented farmyard manure, except that they were deficient in potash and magnesia, in consequence of the substitution of human urine for that of cattle. The same changes, in fact, had been produced as occur in the fermentation of dung, the length of time during which the experiments lasted compensating for the lower temperature at which they were carried on. The loss per cent. of dry solid matter present, and the amount of brown humus acids formed are shown in the annexed table:—

	Loss per cent. of dry matter introduced.	Brown acids per cent. of organic matter introduced.
No. 1. Without addition.....	53·71	1·386
„ 2. With phosphate .....	57·93	0·924
„ 3. With phosphate and gypsum.....	49·74	traces
„ 4. With phosphate and car- bonate .....		
„ 5. With carbonate.....	56·35	0·924
„ 6. With gypsum .....	58·00	0·963
„ 7. Without addition.....	52·61	traces
	56·20	1·309

Gypsum, therefore, in the proportions used, almost totally prevents the formation of the brown humus acids.

The amount and distribution of the nitrogen present in the materials and in each fermented sample, are shown in the annexed table :—

		Nitrogen, grams.			
		Ammoniacal.	Nitric.	Organic.	Total.
Materials of Experiments 1—6	{ straw.....	none	none	0·374	0·374
	{ droppings..	none	none	0·645	0·645
	{ urine.....	2·832	none	0·096	2·928
	Total.....	2·823	none	1·115	3·917
Manure No. 1	{ liquid.....	0·698	none	0·163	0·861
	{ solid .....	0·719	none	1·655	2·374
Total.....		1·417	none	1·818	3·235
Manure No. 2	{ liquid.....	0·644	none	0·143	0·787
	{ solid .....	0·787	none	1·541	2·328
Total.....		1·431	none	1·684	3·115
Manure No. 3	{ liquid .....	0·388	0·044	0·065	0·497
	{ solid .....	0·421	none	1·490	1·911
Total.....		0·809	0·044	1·555	2·408
Manure No. 4	{ liquid.....	0·558	none	0·115	0·673
	{ solid .....	0·335	none	1·505	2·040
Total.....		1·093	none	1·620	2·713
Manure No. 5	{ liquid.....	0·350	none	0·119	0·469
	{ solid .....	0·488	none	1·388	1·876
Total.....		0·838	none	1·507	2·345
Manure No. 6	{ liquid.....	0·231	0·066	0·114	0·411
	{ solid .....	0·694	0·000	1·501	2·195
Total.....		0·925	0·066	1·615	2·606
Materials of No. 7.	{ straw .....	none	none	0·748	0·748
	{ droppings .....	none	none	2·582	2·582
	{ urine .....	3·776	none	0·128	3·901
	Total.....	3·776	none	3·458	7·234
Manure No. 7	{ liquid.....	0·332	none	0·300	0·632
	{ solid .....	0·223	none	4·841	5·064
Total.....		0·555	none	5·141	5·696

There is thus in every case a large loss of ammoniacal nitrogen, ranging from 49·47 to 85·30 per cent. of the quantity introduced. On the other hand, there is a gain of organic nitrogen, ranging from 35·15 to 63 per cent. of the original quantity. A portion of the ammoniacal nitrogen has therefore become fixed on the organic matter, mostly in the insoluble form. The following table shows the proportion of original ammoniacal nitrogen which had become thus transformed, and, on balance, the proportion absolutely lost:—

	Ammoniacal nitrogen per cent. of that introduced.		
	Disappeared.	Trans- formed.	Absolutely lost.
No. 1. Without addition .....	49·96	24·82	25·14
„ 2. With phosphate .....	49·47	20·09	29·38
„ 3. With phosphate and gypsum ..	71·43	17·09	54·34
„ 4. With phosphate and carbonate..	61·40	17·83	43·57
„ 5. With carbonate .....	70·41	13·84	56·57
„ 6. With gypsum .....	67·34	19·98	47·36
„ 7. Without addition .....	85·30	44·54	40·76

This important and absolute loss of nitrogen, ranging from 25·14 to 56·57 per cent. of the ammoniacal nitrogen originally present, must be due either to volatilisation of ammonium carbonate or to destruction of ammonia by the fermentative action of microbes. Seeing that the temperature in these experiments was much lower than prevails in a dung-heap, and that evaporation was restricted as much as possible, the author concludes that the loss in actual practice is still larger. A comparison of experiment 7 with experiment 1 proves that this loss is greatly increased by the larger surface exposed to the air in a thin layer of manure.

Of the substances so often recommended to be added to manure-heaps as absorbents of ammonia, it is seen that gypsum, at any rate, exercises a positively injurious effect, whether used alone or in conjunction with mineral phosphate. This effect is accompanied by a slight nitrification, and an almost total absence of soluble brown acids—the liquors in experiments 3 and 6 being almost colourless. The loss of nitrogen is also increased by carbonate of lime.

J. M. H. M.

**Loss of Nitrogen during the Fermentation of Farmyard Manure.** By C. BRAME (*Compt. rend.*, 99, 390—392).—The floor of the stable is dug out to a depth of 0·6—1·5 metre, the sides of the excavation plastered to render them air-tight, a layer of light soil, 0·3—0·4 metre in depth, is placed on the floor, and over this a layer of straw, furze, &c., to a depth of 0·06—0·1 metre. The liquid excrement from the animals filters through the straw, &c., into the soil beneath, which, after a time, becomes black, and forms an excellent

manure. The upper part of the straw remains dry, and the health of the animals is improved. By this method the loss of ammonia during fermentation is practically prevented. C. H. B.

**Loss of Nitrogen by Organic Matter during Putrefaction.** By A. MORGEN (*Landw. Versuchs-Stat.*, **30**, 429—436).—The author refers to König's researches on this subject, with the general results of which he agrees. Nitrogen certainly escapes in a gaseous form which cannot be retained, like ammonia and nitric acid, by ordinary reagents, and he recommends farmers to add either gypsum or earth containing humus to fermenting bone-meal, fish guano, and such like matters, and to keep the heap moist.

The author believes the theory of the process to be that ammonia is formed during putrefaction, in the presence of oxygen. If no absorbent is present, such as gypsum, kainite, earth, &c., and if the moisture is insufficient, the decomposition continues, and the oxygen burns up the ammonia into nitrogen and water; in the presence of suitable absorbents, the process is arrested at the formation of ammonia. The author refers to the researches of Carius, de Saussure, and Armsby, as supporting his view that the process is one of oxidation caused by free access of air to the decomposing mass.

J. F.

**Comparative Nitrifying Action of certain Salts.** By P. PICHARD (*Ann. Agronomiques*, **10**, 302—315).—The salts experimented with were the carbonates and sulphates of potassium, sodium, calcium, and magnesium. Each of these salts was added, in something like the proportion actually found in soils to a mixture of powdered arachida cake with pure siliceous sand, the arachida cake representing the nitrogenous organic matter of soil, and being present in such quantity as to give  $N = 0.15$  per cent. of the mixture. In two instances, the arachida cake was replaced by ammonium sulphate. The mixtures were made up May 30, 1883, and were placed in glass vases and kept moistened with water and sheltered from rain and dust. On August 30, slight nitrification had taken place in the mixtures containing ammonium sulphate, but not in those containing arachida cake. The author attributes this slight nitrification of the ammonium sulphate to simple oxidation. On August 31, about 0.75 per cent. of dry soil was added to each vase in order to start nitrification. On March 15, 1884, the quantity of nitrate formed in each mixture was estimated in an aqueous extract by the indigo process. The percentage of total nitrogen added, which had nitrified by this time, was in the mixture containing potassium carbonate 4.96, sodium carbonate 2.14, calcium carbonate 26.15, magnesium carbonate 24.47, potassium sulphate 12.59, sodium sulphate, 15.61, calcium sulphate 28.82, magnesium sulphate 3.94. In all the above mixtures, the sand employed was coarse. In a similar set of vases in which fine sand was employed, the percentages of total nitrogen nitrified were as follows: with potassium sulphate 20.86, sodium sulphate 24.96, calcium sulphate 46.29, magnesium sulphate 11.55, no salt added, 4.86. The two mixtures containing ammonium sulphate instead of arachida cake yielding the following results: coarse sand with calcium carbonate

3·86 per cent. of the nitrogen nitrified, with magnesium carbonate 3·18 per cent. The remainder of the ammonia in both these cases had disappeared, the author supposes by conversion into carbonate and volatilisation. These experiments seem to the author to demonstrate the very great superiority of calcium sulphate as a nitrifying agent, and he arranges the salts experimented with in the order of the figures given above.\* He also draws a number of conclusions as to the employment of gypsum and its mode of action as a dressing for soils.

J. M. H. M.

**Comparison of Peat and Straw Litter.** By M. FLEISCHER (*Bied. Centr.*, 1884, 500).—Under nine cattle was strewn, for six days, 250 kilos. of rye straw, and for another six days 187·5 kilos. of peat litter; the cattle were fed with chaff, hay, roots, and grains. The litters yielded, of dry matter, 17·98 per cent. (straw) and 17·11 per cent. (peat). The whole was analysed, and the results are given in the original, which show that the peat is better adapted than the straw to retain the easily soluble nitrogenous matter.

E. W. P.

**Utilisation of Human Excreta.** By K. ENGLER (*Bied. Centr.*, 1884, 411—412).—This paper is a report of the working of a process in use at Freiburg for the treatment of sewage. The solid matters are precipitated by a preparation of manganese, and subjected to a modified process of distillation. The poudrette obtained contains 2·1 to 3·0 per cent. of nitrogen. The water from the operation contained  $12\frac{1}{2}$  to  $15\frac{1}{2}$  per cent. of solid matter with ammonia 0·02 per cent. This water is run into deep pits. As yet, the wells in their neighbourhood have not been contaminated.

J. F.

**Chili Saltpetre for Sugar-beet.** By F. MÜLLER and others (*Bied. Centr.*, 1884, 303).—Müller remarks that the start given to the roots by this manure enables them to resist the attacks of insects. Eggers applied Chili saltpetre to some roots, to others ammonia and phosphates, all of equal money value. All roots suffered from wire-worm, and the saltpetered roots polarised lower in the middle of September, but in October no difference could be distinguished between these and the other crop, except that the yield was higher where the Chili saltpetre had been used. In the succeeding year, as the saltpetre seemed to have lowered the percentage of sugar, part of it was replaced by phosphates, but with a similar result. Kahmann thinks this manure of no great value. Deecke finds the character of the soil an important factor, humous soils requiring ammonia, cold poor soils Chili saltpetre. Weinrich considers the ratio of nitrogen to phosphoric acid may be 2 : 3 without harm ensuing; but all concur in considering that roots manured with Chili saltpetre ripen the soonest.

E. W. P.

\* The author does not seem to have made any examination for *nitrites* in his mixtures. Judging from the extent of nitrification, nitrites must have been present in most, if not in all, and their presence entirely vitiates any conclusions drawn from estimations by the indigo process as to the comparative amounts of nitrogen nitrified.—J. M. H. M.



**Chili Saltpetre for Barley.** By Klawitter (*Bied. Centr.*, 1884, 355).—The application of this manure to barley in Posen was followed by an increased yield when 1 centner per morgen was given at one time; to apply one-half that quantity at sowing and the other half as top dressing was of no advantage. E. W. P.

**Manufacture of Bone-meal.** By J. König (*Bied. Centr.*, 1884, 300—303).—Bone-meal prepared by the old and new methods, removal of the fat by steam, and removal by means of benzene, are compared, with the result that the modern process yields a manure freer of fat, and therefore far more valuable as a manure, and at a lower price; moreover the percentages of nitrogen and phosphates are raised. E. W. P.

**Manurial Experiments at Reims.** By A. Manteau (*Bied. Centr.*, 1884, 383—386).—Ten farmers in the vicinity of Reims agreed to carry out certain experiments on similar lines. The soil of each plot was analysed by Joulie, and ten mixtures of manures were made up and applied, so as nearly as possible to supply the deficiency of fertilising ingredients in the soils. The whole of the plots were then sown with wheat.

Unfortunately the season in which the experiment was carried out was most unfavourable, the winter being very wet, the spring cold, and the summer rainy, so that the results differed very little in all the plots. The results might have been valuable had the season been normal. J. F.

**Manuring Barley.** By H. Wäterling (*Bied. Centr.*, 1884, 305). A mixture of 100 kilos. Chili saltpetre with 50 kilos. superphosphate per morgen brought the highest yield of grain and straw, whilst “super” alone brought less than the unmanured land. This heavy manuring paid for itself and left a surplus, which was not the case with the other plots. E. W. P.

**Potatoes with Lime as a Manure.** By E. Heiden and others (*Bied. Centr.*, 1884, 449—453).—Potatoes are subject to “scab,” of which there are two forms; the one due to *Rhizoktonia solani* (Kuhn) consists of slight elevations on the skin, and does not deteriorate the tuber, whilst the other penetrates deeper, forming depressions penetrating below the skin. The origin and prevention of this latter form of disease is as yet unknown. It has heretofore been ascribed to lime, but fresh lime in the soil does not produce the disease, although in the second year of liming the disease appears. Some (Heiden) hold that the decomposition of the ammonium salts in the soil by the lime is the cause, but the quantity of free ammonia likely to be present (0.003 per cent.) is too small to cause corrosion (Märcker). Schulze states that potatoes manured with farmyard manure are most liable to the disease. Heiden finds that lime greatly assists potatoes, in that it sets free ammonia, which is then converted into nitrates. Märcker adds that this aid to ripening has been often observed, and it also is produced by marling, but he doubts the explanation, for

nitrates retard instead of assisting the ripening process. In the place of Heiden's theory, he proposes as a reason that lime assists the formation of carbonic anhydride; this then sets free a larger quantity of soluble nutriment, and also phosphates, which are known to assist ripening.

E. W. P.

**Beet Culture with Artificial Manures.** By PETERMANN (*Ann. Agronomiques*, 10, 241—262; *Bied. Centr.*, 1884, 370—383).—The experiments detailed in this paper were conducted on the loam soil of Gembloux, containing per hectare to a depth of 20 cm. about 800 kilos. N, 1700 kilos.  $P_2O_5$ , 2000 kilos.  $K_2O$ , 6200 kilos. CaO, and 4400 kilos. MgO. Over 90 per cent. of the phosphoric acid is soluble in ammonium citrate. Nitrogenous manures are usually found very efficacious, whilst potash produces little or no effect. Although the soil is well supplied with phosphoric acid, the repeated use of Chili saltpetre alone as a manure is found after a few years to necessitate the addition of artificial phosphates. The special purpose of the three years' experiments here described was to ascertain the best mode of application of the artificial manure, and the influence, if any, of the mode of application on the elaboration of sugar.

Experiments were made on small plots in 1881 and 1882 with the manure distributed in three different ways—(1) broadcasted and raked in; (2) broadcasted and buried with the hoe; (3) broadcasted and ploughed in. In 1881, the manure consisted of a mixture of sodium nitrate, potassium chloride, and superphosphate; in 1882, the mixture contained sodium nitrate, dried blood, ammonium sulphate, potassium chloride, bone superphosphate, and precipitated phosphate. The results of both years' experiments on the small scale were largely in favour of the deeper mode of burying the manure, and preparations were accordingly made for testing the question on a larger scale in 1883. In order to determine the natural variation in produce of the different plots of the experimental field, ten plots were marked out in 1882, and cropped without manure under precisely similar conditions. The weight of roots obtained on each plot varied from 59,375 to 62,157 kilos. per hectare, mean 60,571; the leaves from 45,162 to 58,005 kilos. per hectare, mean 50,750. The percentage of sugar in the roots varied from 9·13 to 10·07, mean 9·53. Having thus tested the homogeneity of the plots, they were in 1883 again sown with sugar-beet, and manured with a mixture of 500 kilos. (per hectare) of sodium nitrate and 650 kilos. superphosphate. The manure was broadcasted on the plots two days before the seed was sown, and was buried to the various depths required by the harrow or the plough. One pair of plots was left without manure, and to another pair the manure was applied by being drilled in with the seed. The season was much less moist than the two previous ones, and the temperature of the last three months of vegetation was high. The roots were lifted on October 10, and were weighed, and the percentage of sugar subsequently determined in them; the leaves were also weighed. The following table gives a summary of the principal results:—

No.	Mode of manuring.	Roots per hectare.	Leaves per hectare.	Per cent. of sugar.	Sp. gr. of juice.
1..	Unmanured .....	47,827	25,685	11·26	1·0610
10	„ .....	50,792	23,753	11·67	1·0610
2..	Harrowed in .....	59,142	32,320	11·45	1·0601
9..	„ .....	57,592	30,929	11·47	1·0605
3..	Ploughed in to depth of 0·12 m.	63,120	37,457	11·13	1·0593
8..	Do. do.	68,332	31,892	11·49	1·0614
4..	Ploughed in to depth of 0·22 m.	69,574	37,029	10·94	1·0597
7..	„ .. ..	69,617	37,457	11·24	1·0597
5..	Drilled with the seed ..	61,986	35,317	11·19	1·0605
6..	„ „ ..	60,798	42,273	10·77	1·0567

The increase of crop produced by the manure is thus 18·73 per cent. (of the unmanured crop) when the manure is simply harrowed in, 33·29 per cent. when buried to a depth of 0·12 metre, 41·14 per cent. when buried to a depth of 0·22 metre, and 24·30 per cent. when buried between the rows. These results are in the same order as those of the two previous years, and lead the author to the following conclusions:—Artificial manure composed of superphosphate and Chili saltpetre, with or without sulphate of ammonia or organic nitrogen, applied in spring on a loamy soil for the growth of sugar-beet, should be buried by deep cultivation. Burying by the harrow or by superficial cultivation is insufficient to extract from the manure its maximum effect, the absorbent power of the loam being too powerful to allow the nutritive ingredients to descend, even in rainy seasons, to the deep layers of the soil whence the roots of the beet draw their nourishment.

Differences in the mode of applying the manure are without sensible influence on the elaboration of sugar.

Drilling in the manure with the seed delays the appearance of the plant by several days, and may seriously compromise the crop in a spring without rain and with drying winds. Under favourable climatic conditions the plant may regain the lost growth, but will not give the same crop as when the manure is buried by deep cultivation, and the plants have consequently suffered no delay in appearing above ground.

J. M. H. M.

**Manuring of Vineyards.** By A. STUTZER (*Bied. Centr.*, 1884, 413).—Experiments on manuring of vines carried out by the author have proved as successful in 1883 as in previous years, and equally in favour of artificial manures. Of 100 average vines, the yield was—

Manured with stable manure .....	79·4 kilos.
„ artificial manure .....	96·9 „

The artificial manure employed contained 6 per cent. soluble phos-

phoric acid,  $2\frac{1}{2}$ —3 per cent. ammoniacal nitrogen, and 6 per cent. potash; it costs about  $1\frac{1}{2}$  pfenning per vine. J. F.

**Manuring of Hops.** By E. POTT (*Bied. Centr.*, 1884, 412—413). —Hops are considered to require heavy manuring; as a rule, stable manure and the cleaning of cesspits are applied to them. The author, after inspection of the systems pursued in various parts of Germany celebrated for hops, thinks the very high manuring with those organic matters wrong. They increase the yield at the expense of the quality. He thinks they should be used as a well-made and matured compost. Artificial manures should yield good results, 3—6 kilos. bone-meal per square metre with  $1\frac{1}{2}$ —2 kilos. Chili saltpetre in soils poor in phosphates, 6—15 kilos. potassium chloride, with or without Chili saltpetre, in soils poor in potash. J. F.

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## Analytical Chemistry.

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**A Simple Method of Estimating Halogens in the Side-chains of Aromatic Compounds.**—By K. E. SCHULZE (*Ber.*, **17**, 1675—1676).—A weighed quantity of benzyl chloride (or a compound of similar constitution) is introduced into a flask with an excess of a hot saturated alcoholic solution of silver nitrate, an inverted condenser adapted, and the mixture boiled for five minutes. The precipitated silver chloride is then filtered off through a weighed platinum crucible, the bottom of which is perforated and covered with a layer of asbestos, the filtration being assisted by a suction-pump. The silver chloride is washed with alcohol, then with hot water acidulated with nitric acid, and finally again with alcohol; the crucible is lastly ignited and weighed. This method has the advantage of quickness, and is a means of distinguishing between a halogen in a side-chain, and a halogen directly united to an aromatic nucleus. Bromomethylnaphthalene may, for instance, be boiled for several hours with alcoholic silver nitrate without yielding silver bromide.  
A. K. M.

**Determination of Nitrogen by Combustion with Calcium Hydroxide.** By S. W. JOHNSON (*Amer. Chem. J.*, **6**, 60—63).—It has been shown that soda-lime may be replaced by a mixture of sodium carbonate and calcium hydroxide, and it is found that under proper conditions calcium hydroxide alone may be used. Quicklime is slaked, dried, and powdered. Using 0.5 gram of substance containing up to 8 per cent. of nitrogen, a tube of 14 inches is long enough; substances richer in nitrogen require longer tubes. The mixture of substance and slaked lime must not quite half fill the tube, the long anterior layer of slaked lime must be brought to a full red heat before heating the mixture, and must be so kept throughout the combustion; the combustion may be rapid; the tube is cooled

below a red heat before aspirating; cochineal is to be preferred to litmus as indicator in titrating the standard hydrochloric acid used to absorb the ammonia. In the analysis of strychnine, a very small quantity of substance and a long tube must be taken. A number of test analyses are given proving the accuracy of the method.

H. B.

**Estimation of Ammoniacal Nitrogen in Soils.** By A. GUYARD (*Bull. Soc. Chim.*, **41**, 337—339).—It is proposed to estimate the total ammoniacal nitrogen of soils in the following way, by which not only are the ammoniacal salts separately estimated, but also the nitrogenous organic matter which is readily convertible into ammonia. The soil is boiled successively with water and (1) 10 per cent. of calcium carbonate prepared by precipitation, which evolves ammonia only from ammoniacal salts; (2) 5 per cent. of magnesium oxycarbonate; (3) 2 per cent. magnesium oxide (calcined magnesia); (4) 2 per cent. of calcium oxide (quicklime); (5) 0.5 to 1 per cent. of caustic soda or potash; these reagents decompose successively different kinds of nitrogenous organic matter. Lastly, the nitrogen is estimated by combustion with soda-lime.

W. R. D.

**Estimation of Iodine in Human Urine.** By E. HARNACK (*Zeit. Physiol. Chem.*, **8**, 158—164).—This is a criticism on Zeller's paper. The author concludes from his own determinations that no reliance can be placed on the results obtained by the two direct methods, viz., by precipitation as palladium or silver iodide; he has, however, obtained concordant results with either of the following processes:—1st, evaporating the urine to dryness with excess of soda and igniting, and then precipitating the iodine as palladium iodide in the extract of this residue; 2nd, by igniting the precipitate formed by direct precipitation with dry powdered soda, and then reprecipitating the iodine as before, after acidifying with hydrochloric acid.

To account for the high results obtained by direct precipitation with palladium chloride solution, the author supposes the formation of some double compound insoluble in water (as palladium-iodine-creatinine).

J. P. L.

**Estimation of Iodine in Urine.** By E. BAUMANN (*Zeit. Physiol. Chem.*, **8**, 282—290).—Baumann defends Zeller's results and disputes Harnack's statement that no reliance can be placed on the two direct methods; he also points out that Harnack's high results obtained with palladium chloride solution are most probably due to an admixture of organic compounds consequent on the use of hydrochloric acid, and not to the formation of a double compound.

The whole paper is devoted to a defence, and the conclusions are directly opposed to those of Harnack.

J. P. L.

**Estimation of Chlorides in Dog's Urine.** By v. MERING (*Zeit. Physiol. Chem.*, **8**, 229—234).—Salkowski's modification of Volhard's volumetric method of estimating the chlorides in dog's urine is liable to give too high results in consequence of the presence of compounds containing sulphur (thiosulphuric or thiocyanic acid). To avoid this error, the author precipitates the urine with an excess

of silver nitrate and nitric acid, and then either fuses this precipitate with soda and saltpetre, or warms it with zinc-dust and acetic acid, and estimates the chlorides, in the first case, in the watery extract of the fusion, in the second case in the filtrate after reduction.

The chlorates can also readily be determined by taking another portion of urine and reducing with zinc-dust and acetic acid before precipitation, the difference between the two weights gives the chloride derived from the chlorate. J. P. L.

**Volhard's Volumetric Estimation of the Chlorides in Urine.** By M. GRUBER (*Zeits. f. Biol.*, **19**, 569—570).—If nitric acid be used to decompose the sulphur-containing bodies which occur in dog's urine, the end-reaction is much masked by the deep colour. The best course is to treat the urine with a little zinc and sulphuric acid before titrating. (See also preceding Abstract.) J. P. L.

**Estimation of Phosphoric Acid in Superphosphates.** By E. AUBIN (*Compt. rend.*, **98**, 1591—1594).—The insoluble phosphate in superphosphates is usually estimated by extraction with ammonium citrate solution, either at once, or, if magnesium is present, after previous treatment with water. Treatment with water is effected by triturating the phosphate and digesting with a known volume of water, or by exhausting it repeatedly with successive small quantities of water, but the results obtained by the two methods do not agree. In most cases, the first method gives results which are too high, the error being due to the presence of free acid (phosphoric and sulphuric) which attacks the phosphate during trituration, this effect being greatest with samples which form a paste when triturated, and also to the incomplete extraction of the magnesium phosphate. Joulié's method of treating at once with ammonium citrate solution even in presence of magnesium, also gives results which are too high.

Whenever phosphoric acid is precipitated as ammonium magnesium phosphate in presence of ammonium citrate, account must be taken of the solubility of the precipitate in solutions of this salt. The solubility increases with the concentration of the solution, and by always using the same bulk of liquid, containing the same proportion of ammonium salts, a correction may be introduced. C. H. B.

**Reverted Phosphoric Acid.** By T. S. GLADDING (*Chem. News*, **50**, 16—18; 27—28).—Experiments with natural phosphates and artificial soils have been described (this vol., p. 1075). The natural soils used were light loams, one from the truck gardens of Long Island, New York, one from the cotton plantations of North Carolina, and one from the tobacco fields of Connecticut, taken from plots upon which fertilisers had been spread, and large crops had been grown. The soils were ground to pass a 20-mesh sieve, and 100 grams were taken for each experiment. A solution of an ammoniated superphosphate was prepared, of which 50 c.c. contained 0.284 gram phosphoric acid, and this quantity was added to each portion of soil, the wet pasty mass being exposed in thin layers to the atmosphere for five days. The portions were then divided into four equal parts for digestion with ammonium citrate solution at 40° and 65°, and with

water to determine the amount of phosphoric acid not reverted. Experiment I with Long Island garden soil showed that ammonium citrate solution at 65° dissolved all the phosphoric acid added to the soil, whilst at 40° it failed to dissolve 27·81 per cent. of the acid actually reverted by the soil. Experiment II with North Carolina soil gave the same result. In experiment III with Connecticut soil, the result was as in experiment I, with 29·23 per cent. undissolved at 40°. During two days, the mixture of soil and phosphate was very wet, and represented very wet lands; later it passed through all the stages of drought, but at no time contained less moisture than was observed in the fields during the summer season. Tests made with other portions of these mixtures showed that all the phosphoric acid was dissolved at both temperatures, if kept constantly saturated with water, owing to the ready solubility of all gelatinous precipitates at low temperatures. Whether phosphoric acid exists in the soil in combination with lime only, or also with iron and alumina, has heretofore never been proved by any direct laboratory experiment, because no method of separation was known for these three phosphates in the presence of each other in the soil. The fact that a strongly alkaline ammonium citrate solution rapidly attacks insoluble iron and aluminium phosphates, but dissolves even less of insoluble calcium phosphate than when neutral, constitutes a test for distinguishing these phosphates.

The author cites numerous investigators who have dealt with the question of phosphates in soils; he criticises results obtained by Albert and Volbrecht (Abstr., 1880, 571) from which these authors, with Millot and Joulie (*Ann. Agronomiques*, December, 1880), conclude that the amount of phosphoric acid not dissolved by ammonium citrate solution at 40° had become insoluble calcium phosphate. Had they digested at 65° the discrepancies would have disappeared. It is impossible to conclude otherwise than that a portion of the phosphoric acid was in combination as reverted iron and aluminium phosphates. The physical conditions of iron and aluminium oxides in the soils do not seem to affect the principal result of these comparisons of temperature at which ammonium citrate solution is used. Few deposits of mineral phosphates exist free from iron and alumina. It is evident that superphosphates made from such minerals are undervalued when the reverted phosphoric acid is estimated at 40°, because the oxides dissolved by the sulphuric acid subsequently combine in the superphosphate with their equivalent of phosphoric acid, and the reverted iron and aluminium phosphates thus formed are *not all dissolved at the temperature of 40°*, whereas a slight increase in temperature dissolves them entirely without unduly attacking the *insoluble* mineral. Experiments by Millot, Heyden, Stochmann, and Liebig on the rapidity with which the reversion of phosphates takes place are quoted, and the author concludes that it is evident, from the marked and positive results of these experiments, that the only equitable method of valuing the reverted phosphoric acid of a superphosphate must be based on these facts; that the true method of valuation is that which dissolves reverted phosphates of the same degree of solubility as those



which are formed when a soluble superphosphate is mixed with the soil. The author gives the following method of analysis of superphosphates:—

*Preparation of Sample.*—Pass the sample through a 12-mesh sieve. *Moisture.*—Dry 5 to 10 grams at 100°. *Total Phosphoric Acid.*—Dissolve 2 grams in 200 c.c. flask with 50 c.c. nitric acid, with addition of a little hydrochloric acid if necessary, boil gently for fifteen minutes, cool, and fill to mark, filter, take 50 c.c., add 25 c.c. concentrated ammonia, and then nitric acid to acidity. To the hot liquid add molybdic solution, and allow it to remain for an hour at 65°, filter, wash with ammonium nitrate solution, dissolve on the filter with hot ammonia solution, and wash. Run in magnesia mixture from a burette at the rate of one drop a second, stirring constantly. Allow it to stand several hours, filter, and weigh. *Soluble Phosphoric Acid.*—Rub up 2 grams in a mortar with a soft rubber-tipped pestle, digest in 25 c.c. cold water, decant, add another 25 c.c. water to the residue, digest several minutes, and repeat this five or six times; pass all through a filter, fill up to the mark, and take out 50 c.c. and treat as above. *Insoluble Phosphoric Acid.*—Wash the residue on the filter into a 200 c.c. flask with 100 c.c. citrate solution, cork, and digest at 65° for 30 minutes. Filter the warm solution quickly, and wash with cold water. Return the filter and contents to the same flask, add 50 c.c. nitric acid, boil for 15 minutes, and estimate the phosphoric acid as in the total. *Reverted Phosphoric Acid.*—The sum of the soluble and the insoluble phosphoric acid subtracted from the total will give the reverted. J. T.

**Electrolytic Estimations.** By J. WIELAND (*Ber.*, 17, 1611—1612).—The author has examined the various methods of electrolytic estimations with the view to test their accuracy. Classen's method for the estimation of iron in oxalic acid solution (*Abstr.*, 1881, 1081) gives good results. The method applied to manganese (*loc. cit.*) is less to be recommended, whilst Riche's method, in which a sulphuric acid solution is employed (*Compt. rend.*, 85, 226), gives satisfactory results. Classen's method of separating iron and manganese (*Abstr.*, 1881, 1081; 1882, 896) has been tested with currents of different strengths, but the manganese precipitate always contained a considerable proportion of iron, and his method of separating iron and aluminium is likewise unsatisfactory, some aluminium being thrown down with the iron. Parodi and Mascazini's method of separating lead from an alkaline solution (*Gazzetta*, 8, 6, 255) is not to be recommended owing to the ready oxidation of the lead, whilst the estimation of small quantities of this metal may be effected by Riche's method, according to which a nitric acid solution is used (*Ann. Chim. Phys.* [5], 13, 508). Cadmium may be thrown down in a compact form by a current (0.05 ampère) from a thermopile, the negative electrode being a platinum dish of about 150 c.c. capacity; also by stronger currents from a potassium cyanide solution (*Ber.*, 12, 759), and from a weak sulphuric acid solution (*Amer. Chem. J.*, 2, 41). To estimate bismuth, it must be precipitated by a feeble current (0.01—0.05 ampère) from an oxalic or nitric acid solution. A. K. M.

**Estimation of Calcium in Presence of Aluminium, Iron, Magnesium, and Phosphates.** By A. GUYARD (*Bull. Soc. Chim.*, **41**, 339—340).—Calcium oxalate is appreciably soluble in acetic acid or in alkaline acetates, the amount dissolved being proportional to the quantity of these substances that are present. In order to precipitate calcium from such a solution, it is necessary to add sufficient ammonium oxalate to convert the acetates into oxalates, and even then the precipitation is not complete. It is, therefore, better to modify the usual process for estimating calcium in presence of aluminium, iron, &c., by adding sufficient ammonium citrate to keep these substances in solution, and then to precipitate with ammonium oxalate, when the calcium is entirely removed. In presence of magnesium, the operation should be conducted at 70—80°, at which temperature the ammonium magnesium phosphate is soluble. Where silica is present, it sometimes happens that it is also precipitated, carrying with it traces of iron and aluminium, in which case it is necessary to purify the calcium oxalate. When the calcium oxalate has been separated, magnesium or phosphoric acid may be determined in the filtrate and by the usual methods. W. R. D.

**New Method of Estimating Carbon in Steel.** By ZABOUDSKY (*Bull. Soc. Chim.*, **41**, 428—433).—The combined carbon in cast iron, steel, &c., is most accurately estimated by means of a mixture of copper sulphate and sodium chloride. Instead of adopting the usual method of using aqueous solutions of these salts, the author recommends the following plan as quicker and easier. A dry mixture is prepared by evaporating solutions of these two salts to dryness. The finely powdered metal is intimately mixed with about 20 grams of this in a mortar, which should be surrounded by water, and sufficient water added to the mixture to form a pasty mass. After triturating for about half an hour the contents of the mortar are transferred to a beaker, the mortar being washed out with a solution of ferric chloride (25 per cent.). After the addition of some hydrochloric acid the liquid is heated for about three-quarters of an hour, and the precipitate filtered off, dried at 125—130°, and weighed. The results agree very well with those obtained by the older method. The residue, however, is not pure carbon, but a hydrate of that element, and if it is calculated as pure carbon the result is an error of about 35 per cent. on the total quantity. The author has, therefore, determined the coefficients which express the quantity of pure carbon in the residue. These were deduced from a number of experiments with different specimens of cast iron, steel, &c. The results of these analyses, which are tabulated in the paper, lead to the following coefficients :—

Pure specular cast iron containing no manganese .....	0.720
Ferromanganese .....	0.700
Ferromanganese (specular).....	0.685
White cast iron.....	} 0.710
Pure grey cast iron (Bessemer) .....	
Grey cast iron slightly impure, combined carbon low....	0.655

Cannon and gun steel (about 0·5 per cent. of carbon)....	0·660
Hard steel .....	0·675
Swedish iron .....	0·690

The author states that the copper mixture method is more accurate than either the iodine or colorimetric methods of Eggertz. The quantity of pure carbon contained in the iodo-carbon residue of the first process is often much less than the reputed amount (60 per cent.). In the case of Swedish iron, the author found in two different residues 50·9 per cent. and 48·6 per cent. of pure carbon. The second method requires much practice, and does not give comparable results with metals of different origin.

W. R. D.

**Estimation of Chromium.** By H. BAUBIGNY (*Bull. Soc. Chim.*, 41, 291—301).—The usual process for estimating chromium by precipitation as trioxide is inaccurate, owing to the facility with which this compound combines with metallic oxides, which are consequently precipitated with it. The author strongly recommends Storer's process, in which the chromium is oxidised to chromic anhydride by means of nitric acid and potassium chlorate. Chromium is separated from iron or aluminium by first oxidising with nitric acid and potassium chlorate, and adding to the cold liquid a slight excess of hydrogen sodium carbonate, when the iron or aluminium is precipitated, and after washing with a dilute solution of the carbonate is dried, ignited, and weighed in the usual manner. Ammonia cannot be used as the precipitant, for by the action of the oxides of chlorine on it compounds are formed that reduce the chromic anhydride, and the trioxide is precipitated. The chromium is estimated in the filtrate by acidifying with sulphuric acid, adding ammonia, and saturating the liquid with hydrogen sulphide. After boiling, the chromium hydroxide is collected and washed. To completely free it from alkalis it is dissolved in hydrochloric acid, and reprecipitated in the cold with ammonia. Any iron that may have escaped precipitation can be recognised in the precipitate by oxidising it with nitric acid and potassium chlorate, evaporating to dryness at 100°, and after dissolving the residue in a few drops of water, precipitating the iron with ammonia. In presence of alkalis, the same process may be followed, but the chromium oxide should be tested for alkalis by strongly heating, when a chromate is formed and can be recognised in the usual way. When the quality of alkali is large, a loss may occur from the volatilization of chromic anhydride, accompanied by reduction and deposition of chromium trioxide in a crystalline form. The author has noticed that this occurs when a dichromate is heated for some hours at a red heat. In cases where chromium occurs alone, it is estimated by precipitating as lead chromate with lead acetate. Precipitation as mercurous chromate is not accurate in presence of ammoniacal salts, particularly the nitrate, as the chromic anhydride is more or less reduced.

W. R. D.

**Estimation of Arsenic.** By C. HOLTHOF (*Zeitschr. Anal. Chem.*, 1884, 378—390).—The gravimetric estimation of arsenic when it is

present as arsenic acid, and especially when it is weighed, as customary, as ammonium magnesium arsenate presents so many difficulties, and requires so much attention, that the author examined a method first proposed by Mohr, but afterwards abandoned by him, and which consists in the reduction by  $\text{SO}_2$  and titration of the arsenious acid produced by standard iodine. Very careful experiments established that on evaporating arsenic acid with hydrochloric acid to dryness, no trace of arsenic is volatilised, and that on subsequent addition of abundance of sulphurous acid solution the arsenic acid is completely reduced.

The author operates as follows: in case of precipitates containing  $\text{As}_2\text{S}_3$  and sulphur, he oxidises with  $\text{HNO}_3$  or  $\text{HCl}$  and  $\text{KClO}_3$ , evaporates to dryness, adds 300 c.c. of strong sulphurous solution, heats on the water-bath for about two hours, expels the acid by subsequent boiling down to about one half, and after cooling neutralises with acid sodium carbonate, and titrates with iodine. The reagents used must be quite pure, and atmospheric dust must be carefully excluded. The results are quite accurate. O. H.

**Analysis of Type Metal.** By F. WEIL (*Zeitschr. Anal. Chem.*, 1884, 348—349).—2 grams of the alloy are heated in a flask with nitric acid, the excess of the acid is removed, hydrochloric acid is added, and the mixture is boiled until iodised starch-paper is no longer affected. The solution is made up with tartaric acid solution to 200 c.c. In 10 c.c. of this, the antimony is titrated with stannous chloride (Weil's method, "Fresenius' Quantitative Analysis," 6 ed., p. 542).

2 grams of the metal are oxidised with nitric acid, and the mixture of  $\text{SbO}_4$  and  $\text{SnO}_2$  weighed together, the tin being obtained by subtracting the amount of antimony previously found. The lead is estimated in the filtrate in the usual manner.

The object of the method is to avoid the troublesome separation of antimony and tin. O. H.

**Estimation of Molybdenum and Tungsten.** By O. v. D. PFORDTEN (*Chem. News*, 50, 18—19).—1. *Gravimetric methods.*—The author finds that the reduction to metal can be effected in a crucible, with a perforated cover, by means of a good gas-blast. He uses a platinum crucible and passes in a current of hydrogen through an earthen tube. In the analysis of ammonium molybdate, he heats the sample in the crucible at  $170^\circ$  for some hours in an air-bath, thus avoiding spirting. If the temperature is raised higher, say to  $200^\circ$ , there is a slight loss by sublimation. The crucible is then heated gently in a slow current of hydrogen to superficial reduction. In order to guard against possible loss by sublimation, the aperture of the gas delivery pipe is wrapped in a sheet of platinum, running to a point below and fitting into the aperture of the lid, with which it is weighed. After the heat has been gradually raised, the complete reduction is effected in the highest heat of a good gas-blast in a strong current of hydrogen. This method is applicable for all neutral solutions containing molybdic acid, if combined with precipitation by mercurous nitrate as proposed by H. Rose. The cold

concentrated solution, exactly neutralised and freed from carbonic acid, is mixed with excess of the nitrate, and filtered after a few hours. Particles which adhere to the beaker are dissolved off with hot nitric acid and evaporated in a platinum crucible. The main precipitate, when dry, is separated from the paper and placed in the crucible. The portions adhering to the paper may be rinsed into the crucible with hot nitric acid; or the filter is carefully folded up and ignited, so that the particles may be reduced by the carbonaceous matter before molybdic acid can sublime away. The reduction to metal is then effected as above. For the analysis of acid solutions containing molybdic acid, the reduction of molybdenum trisulphide to the bisulphide is recommended as described by Liechti and Kempe. It requires more time than the reduction to metal, and the conclusion of the reduction is not so distinctly marked. The bisulphide obtained must not be too strongly ignited in the hydrogen current.

The gravimetric determination of tungsten is much less difficult. The method of Berzelius—precipitation with mercurous nitrate—is convenient and gives good results. Scheele's method—evaporation of the solution with hydrochloric acid, exactly as for silica—is also good.

2. *Volumetric methods.*—The solution of the salt is mixed, for molybdenum, with 50—60 c.c., and for tungsten with 70—80 c.c. of hydrochloric acid of 27 per cent. There are then added for molybdenum, 8—10 grams, and for tungsten 14—15 grams zinc in the form of rods, and in as large pieces as possible. The solution may contain 0.3 gram molybdic oxide, or 0.1 gram of tungstic oxide; in the latter case, the solution is previously heated on the water-bath, and the hydrochloric acid and zinc are then added; the deposition of tungstic oxide in a solid state is thus avoided. Towards the end of the reduction, a little heat may sometimes be applied to the molybdenum solution with advantage. When the molybdenum solution has become yellow, and that of tungsten red, the flask is cooled—in the case of tungsten with especial care. The remainder of the procedure is different. The molybdenum solution is poured into a porcelain capsule containing 40 c.c. dilute sulphuric acid, and 20 c.c. of manganous sulphate solution free from ferrous salt, and containing 200 grams per litre. An equal volume of water is added, and a dilute solution of standard permanganate is run in. The results are accurate:

$$1 \text{ c.c. KMnO}_4 = 0.000752185\text{O} = 0.00451311\text{MoO}_3.$$

The reduced tungsten solution is rinsed quickly into a capsule in which there is an excess of permanganate, 70—100 c.c. dilute sulphuric acid, 40 c.c. manganous sulphate solution, but otherwise no water. Not until the flask has been rinsed out is the liquid diluted to 1 litre. In presence of such large quantities of hydrochloric acid the manganous sulphate exerts its power of transferring oxygen only in concentrated solutions. Quick working is essential. An excess of ferrous sulphate is now run in, and the solution is finally titrated with permanganate.

J. T.

**Analysis of Potable Water.** By W. BACHMEYER (*Zeitschr. Anal. Chem.*, 1884, 353—359).—The author shows that in Kubel-Tiemann's method of measuring the amount of "oxygen absorbed," the length of boiling, and the quantity and concentration of the acid employed, have a material influence on the result. O. H.

**Determination of the Flashing Point of Petroleum.** By J. T. STODDARD (*Amer. Chem. J.*, 6, 18—23).—Beilstein (*Zeitschr. Anal. Chem.*, 22, 309) has come to conclusions differing from those of Stoddard (*Abstr.*, 1883, 383, 517). The method employed is a modification of Liebermann's (*Abstr.*, 1882, 1326).

It is shown that the flashing point does not depend as stated by Beilstein upon the length and diameter of the oil-cylinder employed, so much as upon the dimensions of the vapour space above the surface of the oil. The quantity of oil to be used is 50 c.c., the cylinder, 2.5—4 cm. in width, must then have a vapour space of 6—4 cm., and the continuous air current should be strong enough to maintain a foam of at least 1 cm. By this method, the lowest flashing point which can be accurately determined is obtained; an approximate and a final test are made. H. B.

**Analytical Estimation of the Three Xylenes in Coal-tar.** By A. REUTER (*Ber.*, 17, 2028—2029).—The author disputes the accuracy of the method proposed by Levinstein (*this vol.*, p. 898), as it has been shown by several writers that pure metaxylene cannot be obtained by treating the mixture of xylenes with dilute nitric acid, whilst stronger nitric acid such as is recommended by Levinstein attacks metaxylene, although more slowly than its isomerides. The author has converted 1 kilo. of pure metaxylene by a few successive treatments with nitric acid (2 vol. acid of 1.4 with 3 vol. water) into a crystalline mass consisting of metatoluic acid, together with a small quantity of an aldehyde. Isophthalic acid was not formed. Paraxylene is attacked by ordinary sulphuric acid, although with considerably more difficulty than its isomerides. A. J. G.

**Detection and Estimation of Small Quantities of Carbon Bisulphide in Air, Gases, Thiocarbonates, &c.** By GASTINE (*Compt. rend.*, 98, 1588—1590).—The gas or vapour to be tested is carefully dried, and then passed through a concentrated solution of recently fused potassium hydroxide in absolute alcohol. The presence of even traces of water seriously diminishes the delicacy of the reaction. The alcoholic solution is afterwards neutralised with acetic acid, diluted with water, and tested for xanthic acid by adding copper sulphate.

In order to determine the distribution of carbon bisulphide introduced into the soil (*Compt. rend.*, 1877), 250 c.c. of the air in the soil is drawn by means of an aspirator through sulphuric acid, and then through bulbs containing the alcoholic potash. For quantitative determinations, a larger quantity of air must be used, and the xanthic acid formed is estimated by means of the reaction  $2\text{C}_3\text{H}_6\text{OS}_2 + \text{I}_2 = 2\text{C}_3\text{H}_5\text{OS}_2 + 2\text{HI}$ . The alkaline solution is slightly acidified with

acetic acid, mixed with excess of sodium hydrogen carbonate, and titrated in the usual way with a solution of iodine containing 1.68 grams per litre, 1 c.c. of which is equivalent to 1 mgrm. of carbon bisulphide.

To apply this method to thiocarbonates, about 1 gram of the substance, together with about 10 c.c. of water, is introduced into a small flask and decomposed by a solution of zinc or copper sulphate, the flask being heated on a water-bath, and the evolved carbon bisulphide passed first through sulphuric acid and then into alcoholic potash. In the case of gaseous mixtures of carbon bisulphide, nitrogen, hydrogen sulphide, carbonic anhydride, carbonic oxide, and water-vapour, the gas is passed through a strong aqueous solution of potash, then into sulphuric acid, and finally into alcoholic potash. The thiocarbonate formed in the first flask is decomposed by treatment with copper or zinc sulphate as above, and the xanthic acid obtained is added to that formed in the third flask, and the whole titrated with iodine.

C. H. B.

**Wine Analysis.** By J. NESSLER and M. BARTH (*Zeitschr. Anal. Chem.*, 1884, 318—323).—For the quantitative estimation of magenta in wine, the following modification of Falière's method is recommended: 100 c.c. of the wine are mixed with 5 c.c. strong ammonia, and well shaken with 30 c.c. ether. 20 c.c. of the ether are drawn off and evaporated in a little basin containing a thread of white wool 5 cm. long. Other threads are then dyed with known quantities of magenta, and from the comparison of tints the amount of the added colouring matter in the wine is inferred. As little as 2 mgrms. per 100 litres may thus be determined. The standard woollen threads, fused into glass tubes, and kept in the dark, do not alter in tint when kept.

The authors determine the amount of tannin as follows: 12 c.c. of wine are mixed with 30 c.c. alcohol; pectinous and albuminous substances are precipitated. Of the filtrate, 35 c.c., corresponding with 10 c.c. of wine, are evaporated to about 6—7 c.c., transferred to a conical test-tube tapering from 16 mm. to 8 mm., and divided into  $\frac{1}{10}$  c.c. Sodium acetate and ferric chloride are added, and after 24 hours' standing the precipitate is measured, 1 c.c. corresponding with 0.033 per cent. tannin.

O. H.

**Estimation of the Dry Extract of Wine.** By E. H. AMAĞAT (*Compt. rend.*, 99, 195—197).—The wine is boiled until its volume is reduced to one-half, in order to expel alcohol, and is then brought back to its original volume by addition of water, and its sp. gr. determined. The amount of dry extract in the wine is very nearly, although not exactly, proportional to the difference between its sp. gr. and unity. This method gives strictly comparable results.

C. H. B.

**Estimation of Dry Substance in Wine and Must.** By R. ULBRICHT (*Landw. Versuchs-Stat.*, 30, 425—427).—The saccharimetric tables of Balling, Steinheil, and Schultze-Ostermann agree fairly with each other, and are correct as tested by the author, whose

experiments were carried out on samples free from water, and at a uniform temperature of 15°; the subjoined table shows the close agreement of the results. The author thinks the table could be used to ascertain the amount of dry extract in wines and must from their sp. gr. Wines poor in sugar and containing relatively high proportions of glycerol cannot be so readily estimated, but glycerol in aqueous solutions can readily be valued in this way.

In order to eliminate the probable error in pyknometric estimation of dry substance, the author adds 0.39126 per cent. for every 1 per cent. of glycerol present in the wine; he is engaged on experiments to eliminate similar errors due to acetic acid.

Weight of dry matter per cent.	Brix.	Gerlach.	Chancel.	Schulze- Ostermann. Aromatic extract.	Chancel. Invert sugar.	Salomon. Dextrose.
	Cane-sugar.					

Sp. gr. at 15° C. Water also at 15° C. = 1.

0.5	1.00196	1.00196	—	1.00197	—	—
1.0	1.00393	1.00393	1.00370	1.00393	1.00380	1.00382
5.0	1.01982	1.01981	1.01937	1.01996	1.01967	1.01970
10.0	1.04032	1.04028	1.03985	1.04061	1.04024	1.03983
15.0	1.06155	1.06150	1.06111	1.06200	1.06151	1.06087
19.0	1.07909	1.07903	1.07860	1.07966	1.07890	1.07829
20.0	1.08355	1.08349	1.08313	—	1.08333	1.08273
25.0	1.10638	1.10631	1.10597	—	1.10597	1.10462
30.0	1.13003	1.12995	—	—	—	1.12718

J. F.

**Method for the Determination of the Molecular Weight and Atomicity of the Higher Fatty Alcohols.** By C. HELL (*Annalen*, 223, 269—283).—By heating primary fatty alcohols with soda-lime, hydrogen is evolved according to the equation  $R.CH_2.OH + NaOH = R.COONa + 2H_2$ . The author endeavoured to found a method of determining the molecular weight of the higher alcohols on the measurement of the hydrogen so evolved, but finds that only about 90 per cent. of the hydrogen indicated by the above equation is given off. The cause of this deficiency could not be ascertained. The method can, however, be used in discriminating alcohols from aldehydes, in ascertaining whether an alcohol is primary, and whether monohydric, dihydric, &c. A. J. G.

**Alkaline Bismuth Solution as a Test for Glucose in Urine.** By E. NYLANDER (*Zeit. Physiol. Chem.*, 8, 175—185).—As the determination of glucose in urine with Fehling's solution is liable to error, owing to the presence of other reducing bodies, uric acid, creatinine, &c.; the author has made a series of experiments with the view of ascertaining the conditions under which the above reagent is most sensitive and accurate. He prepares the solution in the same manner



as Almén, except that he substitutes for the strong potash a solution of soda containing different percentages of  $\text{Na}_2\text{O}$ , 3, 6, 7, 12, and 17 per cent. (2 grams of bismuth subnitrate, 4 grams Rochelle salt, and 100 c.c. of soda solution); the undissolved bismuth salt is filtered off. The general results shortly stated are as follows: A solution containing 8 per cent.  $\text{Na}_2\text{O}$ , added in the proportion of 1 part of reagent to 10 of urine, is the most sensitive and gives the best results, 0.025 per cent. of glucose being easily detected. A larger percentage of soda or addition of the reagent is to be avoided. The albumin, in cases of albuminous urine, should first be removed, as if present in quantity it vitiates the result to some extent. The author has made no experiments to determine whether lactose can be estimated in the urine.

J. P. L.

**Volatility of Glycerol at 100°.** By J. NESSLER and M. BARTH (*Zeitschr. Anal. Chem.*, 1884, 323—332).—Dry pure glycerol is volatile to a considerable extent at 100°, the amount of loss varying with the mode of heating, the shape and material of the vessel, and the surface exposed. Thus 1 gram heated in a water-oven in a platinum basin 80 mm. diameter lost during the first two hours 46 mgrms., during the second two hours 29 mgrms., in the three succeeding hours 21 mgrms. The loss on 0.5 gram similarly heated was the same. On the open water-bath, the loss per hour varied from 29 to 39 mgrms. When the vessel holding the glycerol is of glass the loss is less, other circumstances being equal.

When aqueous or alcoholic solutions of glycerol are evaporated, the loss varies both with the strength of the solution and the volume of the water to be volatilised. It is in all cases very considerable.

O. H.

**Valuation of Calcium Tartrate.** By L. WEIGERT (*Zeitschr. Anal. Chem.*, 1884, 357—365).—5 grams of the finely-powdered substance are heated with 30 c.c. of a 10 per cent. potassium carbonate solution for two hours, the solution is filtered, concentrated to 5 c.c., and mixed with an equal amount of strong acetic acid and 100 c.c. of 90 per cent. alcohol. After a few hours' standing, the hydrogen potassium tartrate is separated, washed with alcohol, and titrated with standard alkali.

If calcium carbonate is present at the same time and this has to be estimated, ordinary volumetric methods cannot be employed, and the carbonic acid has to be determined directly by Scheibler's apparatus or some similar method.

O. H.

**Estimation of the Volatile Fatty Acids in Butter Analysis.** By C. E. SCHMITT (*Ann. Agronomiques*, 10, 262—268).—Having in a previous paper recommended Angell and Hehner's process for the estimation of the volatile fatty acids in samples of butter, the author now enumerates some objections to its use, and recommends as more convenient and delicate Reichert's process, carried out with certain modifications, as follows:—

2.50 grams of butter-fat are taken for the analysis. The butter must be purified by drying it, and decanting the melted fat through

a filter, as the presence of salt in the purified fat will cause the results to be too high. The butter is saponified with an alcoholic potash solution, as in Hehner's process, and the saponified solution, which should measure 70—80 c.c., is introduced with some pieces of pumice into the flask of Boussingault's distilling apparatus for the estimation of ammonia. 10 c.c. of medicinal phosphoric acid (sp. gr. 1.45) are added, and the liquid is distilled until the beaker in which the distillate is received is filled up to a mark at 60 c.c. The distillate is then directly titrated with standard sodium hydroxide of normal strength. Four samples of pure Flemish butter required 13.0, 13.50, 14.0, and 14.3 c.c. of soda. Two other samples of pure butter each required 13.5 c.c. soda, but when analysed by Hehner and Angell's process, one gave 89.15 per cent. of insoluble fatty acid, and the other 88.57 per cent. A sample of goat's milk butter tested by Reichert's process required 13.58 c.c. soda, and a sample of ewe's milk butter 13.65 c.c. A mixture of 4 parts oleomargarine with 1 part of genuine butter required 2.7 c.c. The author mentions that in some cases *butyric acid* is purposely added to oleomargarine in concocting artificial butter.

J. M. H. M.

**Estimation of the Fat in Skim Milk.** By W. FLEISCHMANN and others (*Bied. Centr.*, 1884, 336—338).—The estimations made of fat in milk by evaporating with sand or by the aræometric process are very closely concordant, but when the milk analysed has been skimmed there is a large discrepancy between the two methods, the evaporation process being the lowest; if twice the usual amount of sand is used, the results are better, but the difference is even then 0.125 per cent. of the whole; consequently Fleischmann employs plaster of Paris: 10 grams of milk are evaporated down with 35 of plaster of Paris, and then extracted with ether for three hours; the error is thus reduced to 0.05 per cent. In consequence of these results, all early analyses of skim milk must be used with caution. Schrodt and Hansen publish a similar account of their experience with skim milk; and, in addition, Schrodt states that more dry matter is found by employing sand than when the plaster is used, viz., 0.198—0.246 per cent.

E. W. P.

**General Method of Examining Fats.** By HÜBL (*Dingl. polyt. J.*, 253, 281—295).—As the chemical composition of the various fats is very similar, an attempt is rarely made to ascertain their constitution, the examination of the substances which as "natural constituents" accompany fats being considered of more value in judging of their quality. The term "natural constituents" is applied to colouring matters, resins, nitrogenous substances, &c. Owing to the fact that the estimation of these substances is limited in its application, and that the qualitative composition of the various fats is very similar, those methods only are useful which are based on quantitative determinations, whether of chemical or physical nature. Such methods, which the author calls "quantitative reactions," afford valuable indications of the purity of fats, as they are intimately connected with their chemical constitution. Qualitative tests are of

value in doubtful cases, and serve to control the conclusions drawn from the results of the "quantitative reactions." After referring to the ordinary methods employed for the examination of fats, the author gives a detailed account of his process called the "iodine-addition method." This method is based on the following considerations:—Almost all fats contain members of three groups of fatty acids, viz., acids of the acetic acid series (stearic and palmitic acids), acids of the acrylic acid series (oleic and erucic acids), and acids of the tetr-oleic acid series (linoleic acid). Chemically, these groups of fatty acids show characteristic differences in their behaviour towards haloids. Whilst the first group remains unaltered under ordinary conditions, the second group takes up two haloid atoms very readily, and the third group four atoms. Accordingly, members of the first group are recognised as saturated fatty acids; whilst those belonging to the second and third groups are regarded as unsaturated fatty acids. If, therefore, the addition of a haloid to a fat can be effected under circumstances which exclude the formation of substitution-products, and the quantity of haloid added can be determined with certainty, a constant for each fat is obtained, the magnitude of which corresponds with the character and quantity of the unsaturated acids present. Theoretically the following amounts of iodine are absorbed by unsaturated acids in fats:—

Fatty acids.	Formula.	Grams iodine taken up by 100 grams fatty acids.
Hypogoeic acid.....	$C_{16}H_{30}O_2$	100.00
Oleic acid .....	$C_{18}H_{34}O_2$	90.07
Erucic acid .....	$C_{22}H_{42}O_2$	75.15
Ricinoleic acid .....	$C_{18}H_{34}O_2$	85.24
Linoleic acid .....	$C_{18}H_{28}O_2$	201.59

The action of iodine on fats being too slow, an alcoholic solution of iodine in the presence of mercuric chloride was used. This mixture was found to act on unsaturated fatty acids at the ordinary temperature, chlorine and iodine addition-products being formed, whilst the saturated acids remained unaffected. This mixture acts on free fatty acids in a similar manner. The amount of iodine which a fat is capable of absorbing was determined by treating a weighed quantity of the fat with a measured quantity of a standard alcoholic solution of iodomercuric chloride, and estimating the excess of iodine by titration with a solution of sodium thiosulphate. The percentage of iodine taken up by the fat is called the "iodine number." The subjoined table (p. 1437) illustrates the results obtained by treating a number of fats in the above-described manner. In most cases, the fatty acids were separated simultaneously, and their melting and solidifying points determined.

It will be seen that the drying oils give the highest iodine numbers, the non-drying vegetable oils are the next in order, then come the liquid and lardaceous animal fats, and finally the solid fats. The iodine number does not, however, indicate the drying properties of an oil, although with it the extent to which the oil thickens or dries up increases, and the capability to form elaidin diminishes. D. B.

Character of fat.	Name of fat.	Iodine number.	Limits found for iodine number.	Fatty acid melts at	Fatty acid solidifies at	Saponification value.	A solution in equal parts glacial acetic acid is rendered turbid at
Drying oils.....	Linseed oil.....	158.0	156—160	17.0°	13.3°	194.3	—
"	Hempseed oil.....	143.0	—	19.0	15.0	193.1	—
"	Walnut oil.....	143.0	142—144	20.0	16.0	196.0	—
"	Poppy-seed oil.....	136.0	135—137	20.5	16.5	194.6	—
"	Pumpkin kernel oil.....	121.0	—	28.0	24.5	189.5	108°
"	Sesamé oil.....	106.0	105—108	26.0	22.3	190.0	107
"	Cotton-seed oil.....	106.0	105—108	27.7	30.5	195.0	110
"	Arachis oil.....	103.0	101—105	27.7	23.8	191.3	112
"	Rape oil.....	100.0	97—105	20.1	12.2	177.0	Insoluble.
"	Apricot kernel oil.....	100.0	99—102	4.5	0.0	192.9	114°
"	Almond oil.....	98.4	97.5—98.9	14.0	5.0	195.4	110
"	Castor oil.....	84.4	84.0—84.7	13.0	3.0	181.0	Soluble in the cold.
"	Olive oil.....	82.8	81.6—84.5	26.0	21.2	191.7	85—111°
"	Olive kernel oil.....	81.8	—	—	—	188.5	Soluble in the cold.
"	Bone oil.....	68.0	66.0—70.0	30.0	28.0	—	—
"	Lard oil.....	59.0	57.6—60.0	—	—	195.9	—
"	Butterine.....	55.3	—	42.0	39.8	—	—
"	Palm oil.....	51.5	50.4—52.4	47.8	42.7	202.2	23.0°
"	Laurel oil.....	49.0	—	27.0	22.0	—	26.5
"	Tallow.....	40.0	—	45.0	43.0	196.5	95.0
"	Suint.....	36.0	—	41.8	40.0	170.0	—
"	Cacao butter.....	34.0	—	52.0	51.0	—	105.0°
"	Nutmeg butter.....	31.0	—	42.5	40.0	—	27.0
"	Butter fat.....	31.0	26.0—35.1	38.0	35.8	227.0	—
"	Cocanut oil.....	8.9	—	24.6	20.4	261.3	40.0
"	Japanese wax.....	4.2	—	—	—	222.0	—

**Reaction for Pyridine Bases.** By A. W. HOFMANN (*Ber.*, **17**, 1908—1909).—The author some time ago (Abstr., 1881, 921) described a peculiar reaction which takes place when the methiodide of a pyridine is heated with a caustic alkali. A very characteristic odour, probably due to a methylated pyridine, is produced. The author proposes to use this as a test for pyridine bases. A drop or two of the base and the same quantity of methyl iodide are warmed together in a test-tube, then mixed with powdered potash, just moistened with water, and the whole heated, when the characteristic odour is produced if a pyridine-derivative be present. The smallest trace of a pyridine base may be detected in this way. The odour is something like that of a mixture of mustard oil and isonitrile, and also somewhat resembles that given by quinoline bases when similarly treated. It is most characteristic, and when once smelt will never be again mistaken.

L. T. T.

**Estimation of Amides in Vegetable Extracts.** By E. SCHULZE (*Landw. Versuchs-Stat.*, **30**, 459—467).—In continuation of previous experiments, the author examines the different processes; in the present series, he employs sulphuric instead of hydrochloric acid. 2 grams of crystalline asparagine were treated with 5 c.c. of pure concentrated sulphuric acid (= 8.79 grams  $\text{H}_2\text{SO}_4$ ) and about 100 c.c. of water, connected with an upright condenser and boiled for certain periods; on cooling, the fluid was nearly neutralised with soda, leaving but a trace of free acid, made up to 200 c.c. (in two of the experiments soda was not added, but the boiling was continued longer), 40 c.c. were then distilled with magnesia, and the ammonia estimated by a standard solution. The quantity of ammonia obtained by two hours' boiling was so near the theoretical amount that the author believes the whole of the asparagine to have been decomposed. On reducing the quantity of acid, the results were not so accurate, and the boiling had to be prolonged. Experiments made according to Schlösing's method show that when solutions are nearly neutralised with soda, prior to the addition of milk of lime, the ammonia comes off very slowly, not being finished even in 72 hours.

J. F.

**Indigo Assaying.** By C. T. LEE (*Chem. News*, **50**, 49).—For several years, the author has used a method by sublimation, which has been uniformly satisfactory. Indigo-blue sublimes readily, and, by a careful regulation of temperature, can be separated from the other components of indigo, indigo-brown, indigo-red, mucilaginous matter, &c. Platinum trays 7 cm. long, 2 cm. wide, and 3—4 mm. deep, are used. About 0.25 gram of finely-powdered indigo, which has been dried at  $100^\circ$ , is taken. It is spread uniformly and the tray very carefully heated on an iron plate, covering with a flat iron arch when volatilisation commences. The time required is from 30 minutes to two hours. The heat must not be so high as to cause the formation of yellow vapours. The results are constant within  $\frac{1}{4}$  per cent.

J. T.

**Action of Air on Solutions of Tannin and the Estimation of Tannin.** By A. GUYARD (*Bull. Soc. Chim.*, **41**, 336—337).—The

author finds that air which has been purified by passing through a series of tubes containing potash solution, cotton-wool, soda-lime, and calcium chloride, has no action on either concentrated or dilute solutions of pure tannin. The usual decomposition which is noticed when solutions of tannin are exposed to the air, and which results in the formation of gallic acid is, therefore, probably due to atmospheric particles or ferments, which act without the co-operation of oxygen. It is otherwise with an alkaline solution of tannin, which is rapidly attacked by purified air, the tannin undergoing a process of combustion, provided an excess of air is allowed to pass through it. For this reason Terreil's process for the estimation of tannin is only valid in presence of a limited supply of air. The best reagent for separating tannin from gallic acid is a solution of lead acetate acidulated with acetic acid; as it precipitates the tannin only, the lead compound may be collected and decomposed with dilute sulphuric acid, and the filtered liquid titrated with potassium permanganate. The gallic acid may also be estimated in the filtrate from the lead compound by potassium permanganate.

W. R. D.

**Tannin.** By F. MUSSET (*Dingl. polyt. J.*, **253**, 341—343).—The author found two acids in oak-bark which are precipitated by gelatin and oxidised by potassium permanganate, hence the determination in the case of a mixture of both acids is attended with inaccuracies, owing to the difference in the "permanganate values" of these acids. It is therefore proposed to treat the extract of oak-bark with ethyl acetate, and repeat this operation until the clear ethereal solution ceases to give a blue coloration with ferric acetate. The ethyl acetate is said to contain the tannin of oak-bark, whilst the aqueous solution contains the tannic acid of "oak-red." As this method is too lengthy, the author recommends titration with iodine, the mode of procedure being described in detail in the original paper.

German barks contain 7—8 per cent. oak-bark tannin and 6—10 per cent. oak-red tannin. As the latter may be used with advantage for tanning purposes, the valuation of oak-bark according to the percentage of oak-bark tannin, no longer suffices, and it becomes necessary to consider also the quantity of oak-red tannin in the assay of barks.

D. B.

**Estimation of Extract of Malt.** By K. KRUIS (*Bied. Centr.*, 1884, 428).—The author finds different methods of estimation to yield different results; he recommends Stolba's process with slight variations, viz., to digest 100 grams malt in 400 c.c. water for one hour at the ordinary temperature, then heat to 60°, at which keep it for three hours, cool, dilute to 1 litre, and filter, take the sp. gr., calculate by Balling or Schulze's tables the percentage of extract, and multiply by 10.

J. F.

**Testing Sulphured Hops.** (*Bied. Centr.*, 1884, 369).—The hops are to be washed, the wash water treated with zinc and hydrochloric acid in a flask, and the evolved gas to be tested for sulphuretted hydrogen. It sometimes happens that unsulphured hops

yield sulphuretted hydrogen when treated as above. When bleached and unbleached hops are mixed, at least 10 grams must be used in the analysis—the washing does not remove all the sulphur.

To detect sulphurous anhydride in beer and wine, the distillate of their liquors must be treated with iodine, and the resulting sulphuric acid precipitated by barium chloride. E. W. P.

**Estimation of the Total Nitrogen in Urine.** By PATRI and LEHMANN (*Zeit. Phys. Chem.*, **8**, 200—213).—The authors have extended the process Kjeldahl described in the *Zeitschr. Anal. Chem.*, 1883, for the estimation of nitrogen in food-stuffs and organic compounds generally, to the determination of the total nitrogen in urine, fæces, &c. The general mode of procedure is as follows:—A measured or weighed quantity of the sample is boiled in a flask with fuming sulphuric acid until a colourless solution is produced; this is usually complete after two hours. The solution is then oxidised by adding gradually small quantities of powdered potassium permanganate until the solution is of a deep green. After cooling, it is diluted with water, and an excess of alkali is added. The distillation of the ammonia is at once commenced, the distillate being passed into acid, and the ammonia afterwards estimated by any of the usual methods. In order to avoid the violent bumping that usually accompanies the concentration of the alkaline liquid, a current of steam is passed through the flask. By this means the last traces of ammonia can be easily obtained without any fear of bumping. The figures obtained by this process agree very closely with those given by Dumas, or Will and Varrentrapp's method. J. P. L.

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## Technical Chemistry.

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**A Filter yielding Physiologically Pure Water.** By C. CHAMBERLAND (*Compt. rend.*, **99**, 247—248).—The water is filtered under pressure through biscuit porcelain, and is thus obtained entirely free from microbes and germs, although originally very impure. After being used, the filter can be cleaned by brushing and heating to a moderately high temperature in order to destroy the arrested organic matter.  
C. H. B.

**Antiseptic Action of Nickelous Chloride.** By H. SCHULZ (*Bied. Centr.*, 1884, 360).—A solution of 1 gram nickelous chloride per litre preserves fibrin. Solutions of 0.5—5 per cent. strength were employed on *Aspergillus glaucus* sown in bread; these were prevented from growing. The action is referred to the great affinity of this salt for ammonia.  
E. W. P.

**Borax as an Internal Disinfectant.** By E. DE CYON (*Compt. rend.*, **99**, 147—148).—The author some time ago confirmed Dumas' observations as to the antiseptic properties of borax, and showed that



this salt can be introduced into the human body in quantities amounting to 15 grams per diem, without producing any functional disturbance. He now proposes the internal administration of borax (with food, in quantities of about 6 grams per diem) as a preventative against cholera and other epidemics due to microbes. The borax will not only exert a direct action on the microbes in the alimentary canal, but will also be absorbed into the blood and attack the bacilli which have penetrated into it. A solution of borax or boric acid may also be used for washing. During the violent cholera epidemic in Italy in 1864-65, the workmen in the seven boric acid factories at Lardarello escaped the epidemic, whilst a village 3 kiloms. distant lost a third of its population. C. H. B.

**Recovery of Ammonia from the Gases of Coke-ovens.** By C. WINKLER (*Dingl. polyt. J.*, 253, 374—376).—The author doubts the possibility of success in endeavouring to recover ammonia from coke-oven gases by the methods hitherto adopted, in which the recovery of ammonia is added to the ordinary coking process, without attempting to effect an alteration in the same. He suggests that trials should be made with an experimental oven of the ordinary form, and the latter heated by means of a special generating furnace, instead of utilising the hot gases evolved during the process of carbonisation. It would thus be possible to determine the amount of heat required for coking purposes and the conditions under which the best and densest coke is produced and the largest yield is obtained. The properties of the volatile products of distillation could be studied simultaneously, the yield of tar and ammonia established, and experiments be made to ascertain the most suitable arrangement for cooling the gases. It would be interesting also to determine the evaporative power of the hot gases, their fuel value after cooling, and how far it would be practicable to utilise them for heating the coke ovens. Finally, it would be useful to study the question of increasing the yield of ammonia by the addition of alkaline or chlorinating substances to coal.

It has been demonstrated that it is impossible to convert the total nitrogen contained in coal into ammonia by the process of destructive distillation. In carbonising coal containing 1·73 per cent. nitrogen, Foster found 14·51 per cent. of the total nitrogen as ammonia, 1·56 as cyanogen, 35·26 in the gas, and 48·66 in the coke.

Winkler has investigated the manufacture of coke at the Deuben Works, and obtained the following results:—

Composition of the coal carbonised—

C.	H.	O.	N.	S.	Ash.	H <sub>2</sub> O.
58·44	3·75	5·99	1·08	1·92	10·05	18·77

Yield obtained from 50 hectolitres or 4061·5 kilos. coal—

15·0 hectolitres, or	719·5 kilos. good coke.
33·0	„ 1359·5 „ cinder.
2·3	„ 144·0 „ ash.

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50·3 hectolitres, or 2223·0 kilos.

The average composition of the coal, when calculated according to these proportions, gave—

C.	H.	O.	N.	S.	Ash.	H <sub>2</sub> O.
72.88	0.48	2.31	0.56	2.56	18.36	2.85

Hence 100 parts of the above coal yielded—

53.2 parts coke			and	46.8 parts volatile products.		
Containing—		Equal to		Containing—		Equal to
C...	39.91 parts	68.3 p. c.		C...	18.53 parts	31.7 p. c.
H...	0.26 "	6.9 "		H...	3.49 "	93.1 "
O...	1.27 "	21.2 "		O...	4.72 "	78.8 "
N...	0.31 "	28.7 "		N...	0.77 "	71.3 "
S...	1.40 "	72.9 "		S...	0.52 "	27.1 "
H <sub>2</sub> O.	— "	— "		H <sub>2</sub> O.	18.77 "	100.0 "
Ash.	10.05 "	100.0 "		Ash..	—	—
53.20 parts.				46.80 parts.		

It was not possible to determine the amount of nitrogen contained in the volatile products in the form of ammonia.

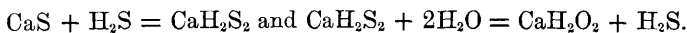
As the annual consumption of coal for carbonising purposes amounts to 18,000,000 tons, it is estimated that 58,600 tons of ammonia could be produced from this quantity, *i.e.*, as much nitrogen as is imported in the form of sodium nitrate from South America.

D. B.

**Production of Ammonium Sulphate and Hydrochloric Acid.** (*Dingl. polyt. J.*, **253**, 350).—On treating ammonium chloride with sulphuric acid, partial decomposition only is effected, an acid residue remaining which contains ammonium chloride. To remedy this, Mond (Ger. Pat., 28,063, November, 1883) adds sufficient sulphuric acid to form hydrogen ammonium sulphate, and neutralises the latter by ammonia or a salt of ammonium.

D. B.

**Recovery of Hydrogen Sulphide from Alkali Waste.** By H. v. MILLER and C. OPL (*Dingl. polyt. J.*, **253**, 350).—It is proposed to treat the residues from soda works with carbonic anhydride or hydrogen sulphide, so as to form a solution of calcium hydrosulphide. This is introduced into iron vessels fitted with stirrers, and heated either by a furnace or with high pressure steam. When the boiling point is reached, decomposition takes place, calcium hydroxide (?) being precipitated and hydrogen sulphide disengaged. Half of the latter is used for obtaining sulphuric acid or sulphur, and the remaining half is employed in the preparation of a further supply of calcium hydrosulphide. The following equations explain the reactions which take place:—



D. B.

**Notes on the Soda Industry.** By SCHEURER-KESTNER (*Bull. Soc. Chim.*, **41**, 335—336).—Reidemeister has obtained from the crude soda solution of Leblanc's process a double sodium calcium

carbonate containing only half as much water of crystallisation as gay-lussite. The compound is found in crystals associated with those of gay-lussite, from which they differ in form. These crystals have the formula  $2(\text{CaCO}_3, \text{Na}_2\text{CO}_3) + 5\text{H}_2\text{O}$ . Some of them were found blackened with ferrous sulphide; others dull and opaque from contamination with silicates of the alkaline earths. W. R. D.

**Analysis of an English Bottle-glass.** By L. GOTTSTEIN (*Dingl. polyt. J.*, **253**, 338).—The author states that although English bottle manufacturers work without the addition of alkalis, the resulting glass resists the action of acid solutions as energetically as alkali glass. At the Stockton Bottle Works the following mixture is used:—Sand 36 parts, clay 18, lime 24, marl 12, and river mud 10. The subjoined analysis indicates that the glass prepared with this mixture has absorbed a small amount of alkali from one of these constituents:—

	$\text{SiO}_2$ .	$\text{Fe}_2\text{O}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .
I.	60·91	3·16	3·39	22·61	6·07	1·10	2·51
II.	61·20	3·29	3·47	22·76	5·73	1·06	2·39

The composition of the glass is remarkable, inasmuch as it is poor in alkalis, but rich in lime and magnesia. D. B.

**Decomposition of Cements by Water.** By H. LE CHATELIER (*Bull. Soc. Chim.*, **41**, 377—379).—When cements are treated with water, not only is the free lime dissolved as is usually assumed, but decomposition of certain metallic compounds containing calcium oxide takes place, which results in the formation of calcium hydroxide. In order to determine the quantity of free lime in cements, they are treated with water in successive quantities so long as the liquid is saturated with lime (1·3 gram in a litre). Under these conditions no decomposition of any calcium compound occurs. The most unstable of these latter compounds is calcium ferrite, which begins to decompose when the liquid contains less than 0·62 gram of  $\text{CaO}$  in a litre. Those cements which contain much free lime “set” but slowly, whilst those which contain little “set” rapidly. In continuing the progressive action of water on cements, it is found that the decomposition of such compounds corresponds with a fixed content of lime, which does not decrease with further additions of water. By titrating the quantity of calcium oxide contained in these solutions, and comparing the results with those obtained from synthetical compounds, the author was able to prove the existence in the cements of the following compounds:—

Grams of $\text{CaO}$ in 1 litre.	
1·3	= $\text{CaOH}_2\text{O}$
1·6	= $\text{Fe}_2\text{O}_3, 4\text{CaO}, 12\text{H}_2\text{O}$
0·2	= $\text{Al}_2\text{O}_3, 4\text{CaO}, 12\text{H}_2\text{O}$

0·05 =  $\text{SiO}_2, \text{CaO}, 3\text{H}_2\text{O}$ .

W. R. D.

**Decomposition of White Iron by Heat.** By L. FOURQUIGNON (*Compt. rend.*, **99**, 237—238).—White charcoal-iron was heated to redness for several days in a vacuum, all traces of air having been displaced by hydrogen. It did not melt nor soften, but became distinctly malleable, and its surface was covered with a dull greyish efflorescence which left a mark on paper. The fracture was sometimes of a uniform black, like that of a lead pencil, sometimes dotted over with regularly disseminated black points of amorphous graphite. The composition of the iron was as follows:—

	I.		II.	
	Original.	Heated 172 hours.	Original	Heated 196 hours.
Combined carbon..	2.959	0.895	2.824	1.159
Graphite .....	0.0	2.061	0.0	1.676
	2.959	2.956	2.824	2.835

When white iron is heated, it is decomposed into graphite and a carbide less rich in carbon.

C. H. B.

**Imitation of Patina.** By E. DONATH (*Dingl. polyt. J.*, **253**, 376—380).—The formation of the so-called "patina" on bronze statues has been the subject of much investigation of late years, in consequence of the fact that most of those of recent origin have become covered with a dense greyish-black film, which gives them an unpleasing appearance. Weber attributes the formation of patina to the composition of the alloy, and recommends the use of tin, suggesting also that the quantity of zinc used should be limited as much as possible. Brühl states that the production of the dark-coloured film is due to the large number of coal fires and furnaces in operation at the present time. His conclusion that this film is free from sulphur is not confirmed by Weber.

Referring to the processes for producing patina by artificial means, the author, after much investigation, found that the treatment of statues with acids (acetic, oxalic, hydrofluosilicic acids, &c.) or ammonia, ammonium carbonate, &c., is attended with practical difficulties. Some time ago Brühl had occasion to make a series of experiments on a bronze statue erected at Aix-la-Chapelle. To restore the statue to its original colour a mixture of 20 parts of acetic acid and 100 parts of fat oil from bones was used. The author in his trials employed oleic acid treated with a small amount of cupric oleate, which is said to prevent the oleic acid from altering. Bone-oil being composed largely of olein, the use of commercial oleic acid suggested itself to the author, inasmuch as the formation of the copper-soap, which is said to be the cause of the green film observed by Brühl, cannot take place until the decomposition of the fat into glycerol and free fatty acid has been effected; moreover, the oxidising action of oleic acid on metals in the presence of oxygen is more powerful. On adding acetic acid to the mixture, it is gradually decolorised, cupric oxide being deposited. It is, therefore, necessary to heat the

same gently, and thoroughly agitate it before use. The objects to be treated are washed repeatedly with a concentrated solution of ammonium carbonate, which produces a bluish-green film. They are then painted with the mixture of oleic and acetic acid. D. B.

### **Toughening Gold (and Silver) in the Melting Crucible.**

By J. C. BOOTH (*Chem. News*, 50, 37—38).—Some brittle coinage gold was toughened as follows:—5400 oz. were melted in a crucible with one or two ounces of soda-ash and anhydrous fused borax. The contents of the crucible appeared as a quiet mass of metal covered with a rather viscid slag, disposed to swell and puff. A few crystals of potassium nitrate, say one or two ounces, were then dropped successively into the centre of the metallic surface, and as they melted their spreading out over the whole surface was aided by the concentric motion of the bottom of a small crucible. The moment the visible oxidising action began to slacken, the fluxed matter was skimmed off by means of a small black lead dipping crucible, as rapidly as was consistent with the care necessary to avoid taking up metal. In this particular case, 1 part of foreign matter was sufficient to impart brittleness to 75,000 parts of good standard gold (900 gold + 100 copper, &c.). By a slight oxidising process, the matter causing brittleness was removed at a trifling cost, without appreciable loss of gold; the standard of the gold was not perceptibly changed by the operation. When the bullion appears to be baser, the only change made in the toughening consists in using a larger amount of soda and borax, and a still larger proportion of nitre. In this case, some of the graphite of the crucible is cut away at the level of the metal, and as the larger bulk of fluxing matter increases the time of skimming, some of the oxidised foreign matter, in the presence of a large amount of metal, and surrounded by graphite, tends to revert to the metallic state. To obviate this, after going through the stronger oxidising process, the oxidation is suddenly fixed by the rapid addition to the floating slag of sand, lime, or bone-ash, which thickens the slag so as to allow more deliberate skimming. The impurities from 75,000 ounces were concentrated into a single button of about 8 ounces. J. T.

**Chemistry of Wine.** By R. KAYSER (*Zeitschr. Anal. Chem.*, 1884, 297—317).—A large number (109) of analyses of wines from the Palatinate, Wurtemberg, the Moselle, Franconia, Italy, Dalmatia, France, and Spain, are given, including estimations of alcohol, extract, ash, acidity, sugar, tartaric, phosphoric and sulphuric acids, lime, magnesia, potash, and glycerol. O. H.

**Malt Extract by Different Waters.** By E. A. MORITZ and A. HARTLEY (*Bied. Centr.*, 1884, 404—406).—Two natural waters and six samples of distilled water, each treated with a special salt, were used to extract albuminoïds from a sample of malt. The malt was of good quality, and the process was conducted in miniature mash-tins, exactly as in commercial way. The extract was filtered from the draff, diluted to 1 litre, 50 c.c. dried at 100° and ignited with soda-

lime. The fresh malt contained N, 2.01 per cent. = albuminoids 12.68.

The results differ in many respects from empirical assertions, and show that the mineral constituents have a considerable influence on the solubility of albuminoid substances in malt; but even those differences do not, in the author's opinion, account for the variety in the finished products, the mineral salts, he thinks, must exert a direct influence on the fermentation.

	Water.							
	Distilled, Na <sub>2</sub> CO <sub>3</sub> added.	Pure dis- tilled.	Dis- tilled & NaCl.	Dis- tilled, MgSO <sub>4</sub> added.	York well water.	New River water.	Dis- tilled with Burton crystals.	Distilled with Ca(NO <sub>3</sub> ) <sub>2</sub> .
No. of experi- ments ....	4	3	3	4	4	2	4	4
Nitrogen ....	0.667	0.71	0.832	0.903	0.910	0.966	0.982	1.098
Average albu- minoids ...	4.220	4.49	5.270	5.710	5.760	6.114	6.220	6.920

J. F.

**Nitrogenous Combinations in Barley, Malt, and Beer Wort.** By H. BUNGENER and L. FRIES (*Bied. Centr.*, 1884, 406—409).—A series of experiments was undertaken to ascertain the influence of the origin of the barley process of malting and mode of brewing on the quality and quantity of the different nitrogenous substances, and the part played by them in fermentation. In these experiments, the nitrogen called albuminoid was the difference between total nitrogen and peptones; these were estimated by precipitation with lead hydroxide, and the amides by precipitation of the resulting filtrate with tannic acid. The first series of experiments was with barley of 1882, from Alsace and Champagne, and pale malt made from it at 65°. Solutions were prepared by steeping the ground barley and malt severally for 18 hours in cold water, with the addition of a little thymol solution, and for the worts at 15 per cent., three-quarters of an hour at 20—70°, and half hour at 70°. The results are, in per cent. :—

	Alsatian.			Champagne.		
	Barley.	Malt.		Barley.	Malt.	
Dry substance, nitrogen .....	1.69	1.58		1.84	1.73	
Nitrogen dissolved .....	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>a.</i>	<i>b.</i>	<i>c.</i>
Total .....	21.0	40.6	36.7	20.6	36.2	36.4
As albuminoids .....	9.5	14.5	10.3	21.1	14.4	10.6
Peptones .....	2.4	3.8	5.0	2.2	2.4	3.5
Amides .....	19.1	22.3	21.4	6.3	19.4	22.3

The other series of experiments yielded similar results.

J. F.

**Hydrogen Peroxide as Beer Preservative.** By WEINGÄRTNER (*Bied. Centr.*, 1884, 428).—The experiments recorded yielded negative results; after 14 days, the flasks of beer treated with hydrogen peroxide were clouded, whilst Pasteurised samples remained perfectly clear. The taste of beer had changed to a flavour of rum; microscopic examination showed much albumin and living yeast cells.

In a second notice, it is stated that nine flasks of beer to which had been added 3, 5, 6, 7, 8, 9, 10 c.c. hydrogen peroxide were carried by the ship "Fulda" to Bremerhaven and back, the voyage lasting a month; they were daily inspected as to colour and transparency, three days after commencement of the voyage, two flasks which were not so treated but kept as control became muddy; the nine remaining clear and bright until returned to New York; four days afterwards they were opened in the laboratory, but during those four days it had become excessively hot and the beer became clouded, the taste and aroma remaining good.

J. F.

**Separation of Sugar from Molasses.** By P. DEGENER and others (*Bied. Centr.*, 1884, 343).—Degener gives the results of numerous analyses of molasses-lime prepared by different processes. Jünemann separates the sugar by gradual addition of milk of lime to boiling dilute molasses and then filtering; 98 per cent. of the sugar present is thus precipitated as lime saccharate, it may then be washed and decomposed by carbonic anhydride. An improvement in the osmotic process is mentioned by G. Stude as employed in France where the organic potash salts are converted into chlorides by the addition of 1—1.3 kilo. ammonium chloride to every 100 kilos. molasses.

E. W. P.

**Quality of the Flour obtained by various Methods of Grinding.** By A. GIRARD (*Compt. rend.*, 99, 380—383).—The flour from the same grain has practically the same chemical composition by whatever method it has been ground, but the extent to which it is contaminated by the nitrogenous *débris* of the envelope of the grains, and by germs, depends on the method of grinding. If the wheat has been ground between metal cylinders, the flour is practically free from these impurities, and yields white bread of excellent quality; if the flour is obtained by progressive grinding between metallic runners, or if the grain has been previously cut and granulated, the flour contains a small proportion of the impurities and the bread is less white; whilst if the wheat has been ground under stones by any method, the proportion of the nitrogenous *débris* and germs is relatively high and the bread is distinctly discoloured.

C. H. B.

**Comparison of Separators.** By FJORD (*Bied. Centr.*, 1804, 339—341).—Three forms of separator were compared, as to their power of separating the cream, and under the various conditions Laval's always left most cream unremoved. The author prefers to use two small machines in preference to one large one.

E. W. P.

**Butter Making and the Souring of Cream.** By KÜHNKE and others (*Bied. Centr.*, 1804, 334—336).—The pleasant aromatic taste of good butter is due to the action of lactic acid on some of the constituents of the milk. Butter for keeping should be prepared from cream only slightly acid, nor should the cream be kept longer than 18 hours at 20° so as to avoid precipitation of casein. According to De la Marvonnais, after the butter has “come” and is in the state of small granules, it should be washed in the churn after removal of the butter-milk; washing it thus removes the casein which is precipitated by the souring of the cream, and is not separated by “working” alone. Calberla by a patent process washes butter in a centrifugal machine; this renders the butter firmer and improves its taste and colour.  
E. W. P.

**Loss of Weight during the Ripening of Cheese.** By B. MARTINY and W. FLEISCHMANN (*Bied. Centr.*, 1884, 341).—Skim milk cheeses will loose by ripening at least 15 per cent. of their weight. Fleischmann publishes a table showing the loss incurred during the ripening of various kinds of cheese; the diminution varies from 12—30 per cent.  
E. W. P.

**Application of Electrolysis in Preparing Indigo-vats.** By F. GOPPELSROEDER (*Dingl. polyt. J.*, 253, 245—252, and 381—385).—In furtherance of his former researches on the use of electrolysis in preparing indigo-vats (this vol., p. 942), and in consequence of a publication by Wartha, the author has conducted a series of experiments with indigo-paste and indigo-vats of different concentrations, such as are employed in dye works, the object being to study one or two points in dispute between Wartha and the author. Although the former does not dispute the formation of indigo-vats by electrochemical means, the author deemed it expedient to make a number of experiments with samples of indigo of different origin, and mixed with caustic alkalis or caustic lime, employing various apparatus, working with cold or hot solutions, and exposing them to the current for a longer or shorter period. To prepare the indigo-vat, indigo was mixed with a solution of caustic alkalis or lime, heated gently and the current passed in. In former trials, it was found that the hydrogenation of indigo-blue to indigo-white could be effected in the cold, although the quantity of indigo-white thus obtained had not been determined. Recent experiments confirm Wartha's results, who found that the vat produced at the ordinary temperature acts very slowly, the hydrogenation of the indigotin being very imperfect; hence it is necessary to work with hot solutions. At the boiling point, the conversion is effected with great ease; the current should not, however, be allowed to act on the indigo-vat for too long a period, otherwise the indigo-white formed at first is altered, and finally decomposed. The author gives a detailed account of his experiments, accompanied by diagrams showing a series of electrolytic apparatus of simple construction.

In prosecuting these researches, the author discovered a new fact. He found that by producing the indigo-vat direct on the fibre and



exposing the latter to the action of the atmosphere, the indigo-white could be converted into indigotin. For this purpose, finely divided indigo was mixed with caustic alkalis and the fabric saturated with the mixture; it was then placed on a plate of metal and covered with another plate, the two plates forming the electrodes. The current was now passed through, and in the course of a short time the indigotin was completely converted into indigo-white. The advantage gained by the use of this method is the possibility of producing new colours on certain parts of the fabric, and printing reserves for white or other colours on the material before it is subjected to the electrolytic treatment.

D. B.

**New Mode of Treating Casein.** By A. DOLLFUS (*Dingl. polyt. J.*, **253**, 351).—The author proposes to treat casein with nitric acid, nitrocasein being formed, which may be used very advantageously for the fixation of colours. Nitrocasein, when dyed on cotton, yields a yellow-drab colour, which resists the action of chlorine and extreme soaping.

D. B.

**Artificial Blue Colours.** By W. ROSPENDOWSKI (*Chem. News*, **50**, 84—87).—In order to ascertain if the dye is homogeneous or a mixture of several colouring matters, the author recommends that a little of the powder should be sprinkled on cold water, when coloured veins will descend from each particle (if the dye is soluble in water), and these will be of the same or different colours, according as the dye is homogeneous or a mixture.

He then proceeds to give the reactions of the ordinary commercial blue dyes, when treated with sulphuric acid, soda, ammonia, stannous chloride, and zinc powder. The reactions are given for 18 dyes—Extract of indigo; Nicholson Blue BBB; Soluble blue BB; Induline BBB; Blue SS; Marine Blue BB; Solid Blue; Solid Black Blue; Blue-Black B; Neutral Blue; Vat Indigotin; Indigotin for wool; Topping Blue (*Bleu remontage*); Gallocyanin and Solid Violet; Acid Myrtle; Liquid Green B; Solid green B, 2B, and 3B; Liquid Greens, No. 1 and No. 2; all these greens are mixtures of malachite green and Paris violet.

C. E. G.

**Canarine.** (*Dingl. polyt. J.*, **253**, 130—131, comp. this vol., p. 796).—This yellow dye, placed in the market by Durand and Huguenin, of Basle, is the yellow precipitate produced by the action of chlorine or bromine on thiocyanic acid.

Prochoroff and O. Miller prepare it as follows: to 1 kilo. potassium thiocyanate in 1 litre water add 20 c.c. hydrochloric acid, and then 1 kilo. bromine gradually, keeping the mixture cool. The yellow precipitate of crude canarine is dissolved in potash and mixed with alcohol, when a potassium compound is thrown down, which yields pure canarine when decomposed with hydrochloric acid. When dried at 100°, it is a reddish-brown glistening powder, insoluble in water, alcohol, and ether, soluble in concentrated sulphuric acid and in potash solution.

H. Schmid considers canarine to be identical with persulpho-

cyanogen,  $C_3NH_3S_3$ . O. Miller disputes this, asserting that canarine dissolves in concentrated sulphuric acid with evolution of sulphurous anhydride, which is not the case with persulphocyanogen.

To apply canarine, Prochoroff and O. Miller dissolve 1 part in 1 part caustic potash and 20 parts warm water, and add to the brown solution 7 to 10 per cent. of soap, afterwards allowing to cool. Water containing lime or magnesia should be avoided, as these bases throw down the dye. Neither can caustic soda be used, as the sodium compound is insoluble in the cold. The dye is decomposed if it is heated too long with potash. Köchlin boils 100 grams canarine in 1 litre water with 100 grams borax. Hot solutions of canarine in soda can also be employed. The procedure is then similar to that of alizarin dyeing. By thickening the borax solution, printing, and steaming, a pure yellow is obtained. Canarine colours are distinguished for their resistance to light and soap. J. T.

**Auramine.** (*Dingl. polyt. J.*, 253, 86—87.)—This interesting novelty is the first artificial yellow dye which can be fixed on the vegetable fibre with tannic acid like aniline dyes. According to C. Köchlin, a steam colour is prepared of auramine 1 part, tartaric acid 1 part, and tannin 6 parts. If this colour be printed on ordinary textures instead of on those prepared with tin, it becomes perfectly fixed, after steaming, by the usual treatment with tartar emetic. The dye then resists soap. Auramine also becomes fixed on wool, giving colours of great purity. The colours bear light very well, but are sensibly affected by chlorine.

Owing to its property of being fixed by tannin, it can be mixed with other tannin dyes, as, for example, in the production of very yellow shades of malachite green, &c. Auramine can be fixed, under certain conditions, with metallic mordants such as alumina.

Poirrier produces a dye, *jaune solide*, remarkable for purity; it is an azo-dye, which can be fixed by chromium acetate. Like Persian berries, it can be mixed with coerulein, logwood, &c., to produce olive and other tints, also with aniline dyes. Alone, the dye gives orange-yellow shades of considerable resistance to light and soap.

Flavaniline, a third new yellow dye for silk and wool. According to C. Köchlin, in printing it is best fixed with its weight of tartaric acid and magnesium acetate. If cotton goods printed with manganese brown be dyed with flavaniline, a bright brown is produced, as is the case with naphthylamine, only where the brown has been discharged with tin salt a yellow appears. J. T.

**New Coal-tar Dyes and their Preparation.** (*Dingl. polyt. J.*, 252, 519—523.) According to the Farbenfabriken, formerly F. Bayer and Co., a third body has been found in the two monosulphonic acids of  $\beta$ -naphthol, which appears to be a sulphonic acid of  $\beta$ -naphthol, and, like Schaeffer's acid, combines more readily with diazo-compounds than the  $\alpha$ -monosulphonic acid previously described.

A new yellow colouring matter, called "echurin," is obtained, according to the Leeds Manufacturing Company, by mixing 5 parts

picric acid with 3 parts flavin, adding 12 parts nitric acid of 36° B., heating on a water-bath, and evaporating to dryness.

Majert obtains quinoline-derivatives from the nitro- and amido-derivatives of anthraquinone in the same way as from nitrobenzene or aniline. These bodies form yellow colouring matters, whose alcoholic solutions impart a yellow colour to wool and silk, which is very permanent. By converting the dyes into sulphonic acids, they are obtained in a soluble form. D. B.

**Separation of Azo-colouring Matters of Mixed Naphthol-sulphonic Acids.** (*Dingl. polyt. J.*, 252, 440.) Dahl and Co., instead of separating naphtholsulphonic acids and preparing azo-dyes from the pure acids, isolate certain azo-compounds by the different solubility of their alumina, lime, baryta, and strontia derivatives. This is specially applicable to azo-dyes prepared from a mixture of the  $\alpha$ - and  $\beta$ -monosulphonic acid of  $\beta$ -naphthol with diazo-naphthalenemonosulphonic acid and diazo-azobenzenemonosulphonic acid, or in the case of dyes obtained from a mixture of the di- and tri-sulphonic acids of  $\beta$ -naphthol with diazo-naphthalenemonosulphonic acid, diazo-azobenzene, and diazo-azobenzenemonosulphonic acid. D. B.

**Preparation of Red and Violet Dyes.** (*Dingl. polyt. J.*, 252, 343.)—When  $\alpha$ -naphthol is introduced into cold fuming sulphuric acid, a new  $\alpha$ -naphtholsulphonic acid is produced, in addition to that described by Schaeffer. A new acid is obtained also when the diazo-compound of Piria's naphthionic acid prepared by sulphonating naphthylamine is decomposed by boiling it with acidulated water. Whilst by the action of diazo-compounds on Schaeffer's acid, orange and brown dye-stuffs are produced, the monosulphonic acids which are obtained from  $\alpha$ -naphthol in the cold, and from Piria's naphthionic acid, yield ponceau to cherry-red dyes (Verein chemischer Fabriken, Mannheim).

By the action of phosgene on dimethylaniline and diethylaniline, the corresponding acid chlorides and ketone bases are formed, and, as bye-products, violet colouring matters. According to the Baden Aniline and Soda Works, the formation of these dyes becomes the primary reaction when the action of phosgene on the tertiary bases is assisted by some energetic condensation agent, such as aluminium chloride. It is thus possible to obtain from dimethylaniline and diethylaniline violet dyes of the triphenylmethane group; also similar colouring matters, by extending this reaction to a large series of tertiary aromatic monamines. D. B.

**Manufacture of Lignose (Wood Cellulose).** (*Dingl. polyt. J.*, 252, 323—328.)—In order to remove the difficulty attending the "sulphite boiling" process, viz., the evolution of sulphurous anhydride and the contamination of the surrounding atmosphere with this gas, Graham proposes the use of the monosulphites of potassium, sodium, magnesium, &c. For this purpose a solution of the monosulphite or a suitable combination of any of them is introduced into the boiler, and when the gases contained in the wood and the boiler

have been driven off by heat, sulphurous acid in the gaseous or liquid state is injected. Instead of the introduction of sulphurous acid alone, it may be injected in combination with potassium, sodium, or magnesium. An excess of acid should be employed, but not sufficient to form in the boiler a solution of acid sulphites.

In bleaching the fibres from vegetable substances, Graham has patented a process which consists in bringing sodium or potassium nitrate in solution into contact with the fibrous substances, being treated either at the same time as or subsequent to their treatment with the ordinary chlorine bleaching agents.

Pictet and Brélaz show that the high temperature (120—140°) used in the process for preparing lignose converts all gummy and resinous substances into tars, which interfere with the subsequent bleaching operations. They therefore recommend the use of an aqueous solution of sulphurous acid, which is said to dissolve the incrustating substances of the wood at a low temperature, so that a larger yield of cellulose is obtained, and the bleaching is facilitated.

For the preparation of cellulose from wood, straw, &c., 100 kilos. wood are brought into a wrought-iron boiler, and treated with an aqueous solution of sodium sulphide (10° B.) containing 30 kilos. pure sodium sulphide. The mixture is then heated for 6—10 hours, at a pressure of from 5—10 atmospheres.

Blitz boils wood for 3—4 hours in a closed vessel, at a pressure of 4 atmospheres, with a solution containing 6 kilos. sodium sulphide, 3 kilos. caustic soda, and 1 gram ammonium vanadate. D. B.

**Explosives.** (*Dingl. polyt. J.*, 253, 70—77.)—Recently, much has been said about panclostite, an explosive patented by E. Turpin, but not to be confounded with a compound of the same name previously described (*Dingl. polyt. J.*, 252, 153). Turpin's procedure rests on the application of nitrous acid, with which the liquid hydrocarbons (petroleum, toluene, xylene, naphthalene) nitrogen-compounds of the tar-derivatives (nitrobenzene, nitroxylenes, aniline nitrate, nitraniline), and various fats (suet, butter, linseed oil) gives mixtures of explosive substances. The fatty bodies are first nitrated by means of nitrous acid, and warmed on the water-bath to expel nitrous fumes. These nitrated fatty bodies, or the other non-nitrated compounds, are mixed with 1—2 parts of nitrous acid, in order to produce the explosive; this product is absorbed by porous substances, as in the case of nitroglycerol, and made up into air-tight cartridges of metal or glass. When ignited, panclostite burns quietly, and only detonates under a percussive impulse. The addition of carbon bisulphide makes the compound more easily explosive, whilst increase in the nitrous acid increases the explosive power. Panclostite, however, appears to be too unstable and uncertain for practical work. J. T.

## ERRATA IN VOL. XLIV.

Page	Line	
733		in the Abstract " <b>Mononitroresorcinol</b> ," read "mononitro- soresorcinol" for "mononitroresorcinol" throughout.
785	15	from bottom, <i>for</i> "Freih" read "v. d. Pfordten."

## ERRATA, VOL. XLVI.

Page	Line	
164	17	from top, <i>for</i> "Zephroïte" read "Tephroïte."
168	18	„ bottom, „ "A white, opaque, and silky crystalline precipitate" read "A white, opaque and a silky, crystalline precipitate."
257	5	„ „ „ "Trimethylamine" read "triethyl- amine."
781	13	„ top, „ 82·86 read 82·85.
„	16	„ bottom, „ "coal of" read "cannel coal of."
„	18	„ „ „ "cannel coal of" read "coal of."
882	15	„ top, „ } "Compt. rend., 89," read "Compt.
„	8	„ bottom, „ } rend., 98."
1156	11	„ „ „ "by its complete insolubility in boiling alcohol" read "as it crystallises from its solution in concentrated nitric acid, whilst the $\beta$ -compound remains dissolved."